ELECTROCHEMICAL TREATMENT OF WATER CONTAMINATED WITH METHYLORANGE

MARTIN VALICA, STANISLAV HOSTIN

Department of Ecochemistry and Radioecology, Faculty of Natural Sciences, University of SS. Cyril and Methodius in Trnava, Nám. J. Herdu 2, Trnava, SK-917 01, Slovak Republic (martin.valica.mv@gmail.com)

Abstract: This study examines electrochemical degradation of water artificially contaminated by azo dye Methyl Orange (MO). Degradation is based on chemical electro-oxidation of MO molecules. Graphite was used as an electrode material for electrochemical oxidation of MO. In this work, the different operative parameters (electric current, NaCl content) and their effect on effectiveness as well as the treatment time/duration of MO degradation were tested. The highest dye removal (91.0 %) was obtained during the electrolysis at current density 3.032 mA/cm^2, electrolyte with the content of NaCl 4 g/dm^3 (NaCl) and the treatment time 35 min.

Key words: dyes, Methyl Orange, electrochemical oxidation, active chlorine, water contamination, degradation.
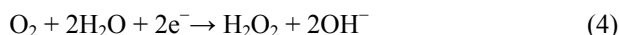
1. Introduction

Environmental pollution is a global issue. Textile and printing industries are regarded as the most polluting sectors due to their high discharge volume of dyes-contained wastewater, especially azo-dye with approx. 50–70% of the world dye production. These dye effluents are typical by high organic content, intense color and stable chemical structure due to the presence of azo groups in molecules (KAR *et al.*, 2009; MA and ZHOU, 2009; SHAKIR *et al.*, 2010). Wastewater contained dyes can be toxic and mutagenic. Dyes are highly soluble and persistent in polluted water, because they have long degradation time in the environment (AZAMI *et al.,* 2011).

Pretreatment processes have been found important for significant decrease of organic content and color of dye polluted water. The commonly used pretreatment processes include adsorption, chemical oxidation, and ion exchange (KONG *et al.,* 2011). In recent years, electrochemical treatment processes, especially electrochemical oxidation and electrocoagulation, have been studied as alternatives for degradation of various types of organic pollutants in wastewater (PANIZZA *et al.*, 2013; ARAUJO *et al.,* 2014; SIRÉS *et al.,* 2014; BRILLAS and MARTÍNEZ-HUITLE, 2015; SANTOS *et al.,* 2015).

Electrochemical oxidation is especially important because no chemical reagents are used in the process. Electrochemical oxidation is the process of oxidizing pollutants on the electrode surface, directly through the formation of disinfectants such as highly-oxidative oxygen species from water itself (Eq. 1-4) or in combination with substances producing electrogenerated active chlorine compounds (Eq. 5-7) if chloride ions are present in the solution (SIRÉS *et al.,* 2006; CARTER and FARRELL, 2008; CHAPLIN *et al.,* 2009):

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{1}$$

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \tag{2}$$

$$3H_2O \rightarrow O_3 + 6e^- + 6H^+ \tag{3}$$

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \tag{4}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{5}$$

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \tag{6}$$

$$HOCl \rightarrow H^+ + OCl^- \tag{7}$$

Electrochemical degradation as a pretreatment process significantly improves further water purification. Moreover, the simple setup, easy control, ambient operation and complete degradation during electrochemical enhanced process further broadens its attractiveness for practical implementation (BONIN *et al.,* 2004; VALERO *et al.,* 2010; SALA and GUTIERREZ-BOUZAN, 2012).

The aim of this work is to study the different electrochemical degradation behaviours of the model azo-dye on carbon electrodes through investigation of main operative parameters (time of electrolysis, amounts of NaCl in electrolyte and current density). Methyl Orange (MO) was selected as the model azo-dye (containing –N=N– bonds), because it is widely used in the textile industry and has harmful effect on human health. To avoid the accumulation of MO in the environment it is necessary to develop effective methods for degradation or mineralization of MO (AZAMI *et al.,* 2011; ZHOU *et al.,* 2011; RAMÍREZ *et al.,* 2013). These requirements may be provided by electrochemical water treatment, because organics can be completely mineralized to carbon dioxide by the hydroxyl radical and active chlorine is generated during the electrolysis of NaCl in the water solution.

2. Materials and methods

2.1 Chemicals

Methyl Orange (MO) dye (Lachema, Czech Republic) and NaCl (purity > 98 %; Chemapol, Czech Republic) of analytical grade were used in experiments. The chemical structure of MO is shown in the Fig. 1.All solutions were prepared in distilled water with the conductivity 10 µS/cm.
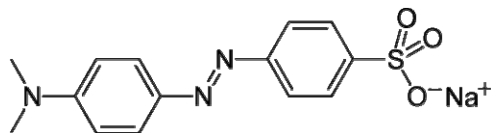

Fig. 1. Chemical structure of Methyl Orange.

2.2 Experimental device and procedures

Electrochemical experiments were carried out at laboratory temperature in an undivided electrochemical cell under conditions of batch system. Equipment for

electrochemical water treatment is shown in the Fig. 2. The cell contained two graphite electrodes (Elektrokarbon, Slovak Republic) positioned vertically and parallel to each other with an inter-electrode distance of 1.5 cm. The geometric area of the anode and the cathode was 15.7 cm^2. The model wastewater was prepared with the known content and volume of MO solution and the supporting electrolyte of NaCl. The solution was stirred by circulation performed with a pumping device to maintain a uniform concentration of the electrolyte solution within the system. Also, this device pumped wastewater into the spectrophotometer (SPEKOL 11, Carl Zeiss JENA, Germany) to analyse the remaining concentration of MO by recording results into a computer in time intervals of two seconds. Because output values of spectrophotometer were in electric current (measured by digital VOLTCRAFT VC820 with software Digiscop for Windows ver. 2.06), it was necessary to convert these values to absorbance using the calibration curve between these two variables.
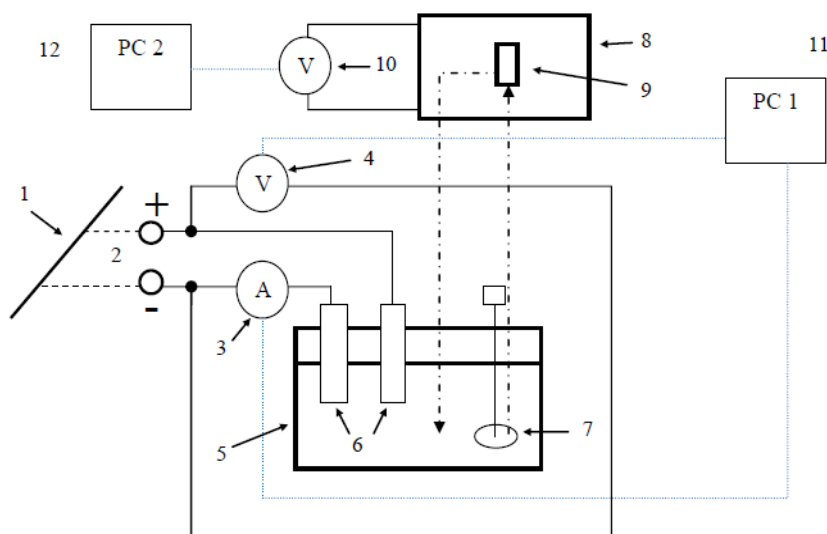

Fig. 2. Electrochemical wastewater treatment equipment: 1. photovoltaic cell/; 2. laboratory electric source; 3. amperemeter; 4. voltmeter; 5. electrolytic cell; 6. graphite electrodes; 7. pump; 8. spectrophotometer; 9. flow cuvette; 10. voltmeter; 11., 12. PC for recording results.

All degradation processes were carried out under the galvanostatic conditions for the wastewater volume of 4 dm^3. The electric power was supplied with a regulated DC power supply (Elektrolyser, Veb Mlw Labortechnik Ilmenau, Germany). After pH adjustment, the degradation was initialized and the current was set at the desired value. During electrolysis, the values of electric current and voltage transferred through the electrolyte were recorded on a computer in time intervals of two seconds. For this measurement, two separate digital multimeters (METEX M-3850D with software ScopeView ver. 1.06; and AXIO MET AX-18B with software PC Link soft) were used. Electrochemical water treatment was finished, when the lowest and constant values of the absorbance of wastewater were obtained.

2.3 Analytical methods

MO concentrations were measured using the spectrophotometer SPEKOL 11 at the maximum absorption peak of 465 nm. This wavelength was determined from the absorption spectrum of MO in water solution measured with the UV-VIS spectrophotometer (Spectroquant® Pharo 300 Merck, Germany) in the wavelength range between 200 to 800 nm. The decolorization ratio (η) was calculated using the following equation (Eq. 8):

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (8)$$

where C_0 and C_t are concentrations of model wastewater measured at wavelength 465 nm and at the initial and the given time *t*.

The remaining concentration of MO in wastewater was determined from the equation of the linear dependence between the concentration of MO and absorbance, for solutions with the known concentration of MO ($0.4 - 4.4$ μg/cm^3).

3. Results and discussion

3.1 Effect of current density

The effect of current density on wastewater decolorization was analysed at different current densities within the range of 1.011 - 4.042 mA/cm^2 under the constant concentration and volume of NaCl electrolyte (4 g/dm^3) and the initial content of MO in the wastewater (approx. 4 μg/cm^3). This range of current densities was chosen from point of view of the energy consumption i.e. economic efficiency of water treatment. The dependence of the residual content of MO in wastewater from treatment time is shown in the Fig. 3.
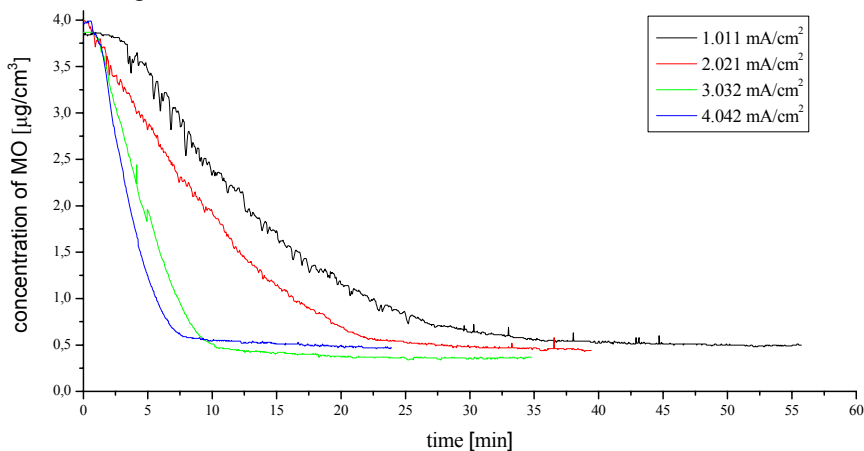

Fig. 3. Electrochemical decolorization of MO under different current densities (conditions of the experiment: initial concentration of NaCl 4 g/dm^3; pH 6).

It is evident that the dye degradation on graphite electrodes was more efficient at higher values of current density. Also, the treatment time needed for electrochemical degradation of MO was shorter at higher current density (Table 1).

As demonstrated in the Table 1 and Fig. 4, the decolorization ratio η linearly increased with treatment time and current density. The key role of current density is shown for instance, at the treatment time of 400 s when under current density of 4.042 mA/cm^2 the decolorization ratio was about 80%. At the same time, decolorization ratio under 1.011 mA/cm^{2}current density was only 18%.

Table 1. Efficiency of MO degradation obtained under various operating parameters.

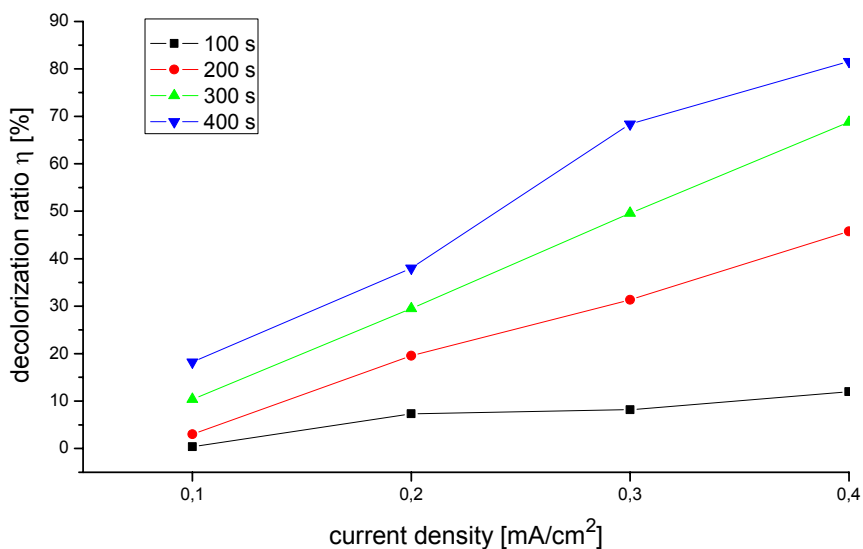| Parameters		Concentration of MO		Decolorization ratioη [%]	Treatment time [min]
Current density [mA/cm^2]	Concentration of NaCl [g/dm^3]	Initial [μg/cm^3]	Final [μg/cm^3]		
1.011	4	3.86	0.50	87.1	55
2.021	2	3.97	0.75	81.3	78
2.021	4	4.00	0.44	89.1	39
2.021	6	3.89	0.43	89.0	32
3.032	4	3.87	0.36	91.0	35
4.042	4	3.97	0.47	88.6	24

Fig. 4. Dependence of the decolorization ratio η from current densities on electrodes, conditions of the experiment: initial concentration of MO aprox. 4 μg/cm^3 and NaCl 4 g/dm^3, pH 6.

Similar results were found in various research papers (MA *et al.*, 2007; CARVALHO *et al.*, 2011; YUSUF *et al.*, 2016), where a slower response of MO to electrochemical decolorization at lower current densities was observed, but an increase of applied current densities caused a sharp increase in the percentage of color removal.

At different condition of current density was reached same level of the total dye removal efficiency (87.1 - 91.0 % dye removal). This could be ascribed to the fact that the amounts of the produced oxidants, such as chlorine, hypochlorite, oxygen species are very similar, however they are produced in different electrochemical treatment times. This assumption is supported by the Faraday's law making known that the amount of electrochemical products is proportional to the current and is constant at a constant applied current (YUSUF *et al.*, 2016).

3.2 Effect of supporting electrolyte

In experiments, NaCl was chosen as the supporting electrolyte to enhance the degradation efficiency and shorten the treatment time according to findings of other authors (PANIZZA *et al.,* 2000; KONG *et al.,* 2009). The different supporting electrolytes such as NaCl, KCl, KNO_3 and Na_2SO_4 were studied by other authors (LORIMER *et al.*, 2001; KONG *et al.*, 2011, YUSUF *et al.*, 2016).Their results showed that the presence of chloride ions played an important role. Almost total decolorization was obtained with KCl, when a very low color removal was obtained with Na_2SO_4 and no decolorization was achieved with KNO_3. Electrochemical degradation of MO was provided by the direct anodic oxidation, but the most important role played the indirect oxidation with active chlorine compounds produced in electrolysis of NaCl/KCl. In the absence of chloride ions, neither any oxidative species are produced nor does any direct anodic oxidation of the dye occur (YUSUF *et al.*, 2016).

In article LI *et al.* (2013) was observed from changes of FTIR spectra evidences of MO degradation and intermediate formation. Most of the characteristic bands of MO, e.g., the characteristic band of benzene rings (1600 cm^{-1}) and the band of N=N (1520 cm^{-1}), significantly decreased or disappeared after 4 h treatment, while two new bands at 1263 cm^{-1} and 800 cm^{-1} appeared. Possible mechanism of electrochemical degradation of MO (Fig. 5) was studied by LC–MS (RAMÍREZ *et al.,* 2013) and GC-MS analysis (DU *et al.,* 2011). Results from LC-MS indicated the formation of seven various oxidation products from the cleavage of the –N=N– group of the dye, followed by deamination, formation of a nitro group and/or desulfonation of the resulting aromatics (RAMÍREZ *et al.,* 2013). In the presence of chloride, the electrolysis was able to oxidise the dye with partial mineralisation of carbon, nitrogen and sulfur into CO_2, NO_3^- and SO_4^{2-}(DU *et al.,* 2011).

Dye removal was found to be dependent of NaCl concentration in electrolyte (initial concentration of NaCl in wastewater was in the range of 2 - 6 g/dm^3) during the experiment with the constant current density (2.021mA/cm^2) and initial MO concentration (approx. 4 $\mu g/cm^3$). These conditions were chosen with the aim to find the correlation between the concentration of NaCl and the treatment time needed for MO degradation.
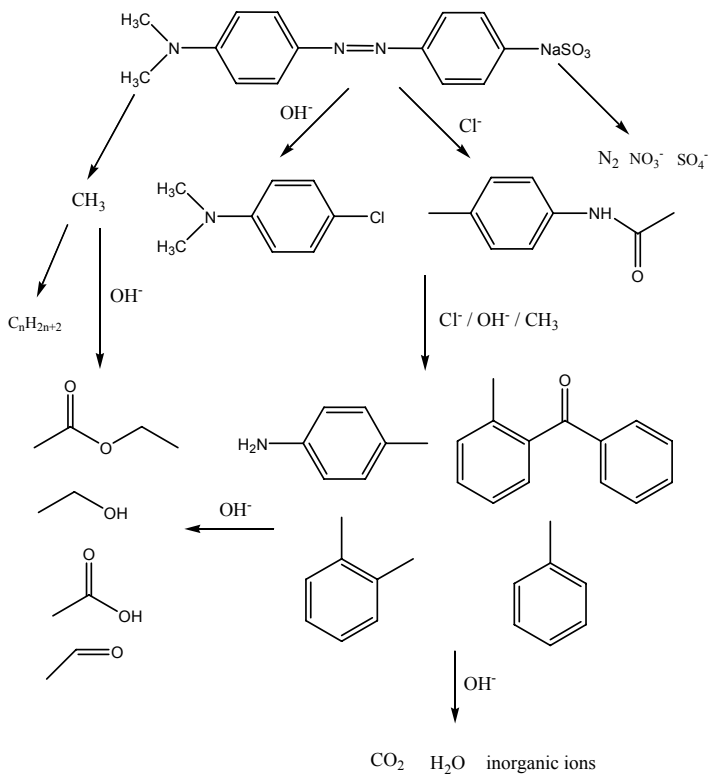
Fig. 5. Proposed electrochemical degradation pathways for MO (adopted from DU *et al.,* 2011).
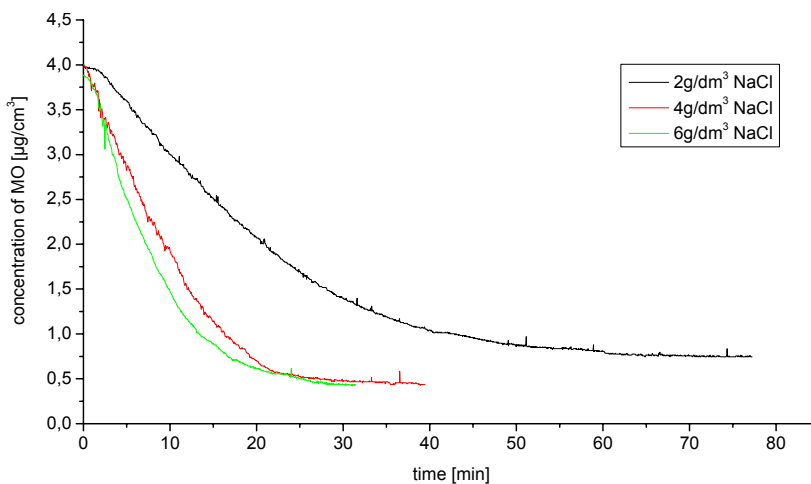

Fig. 6. Electrochemical decolorization of MO at various concentrations of NaCl, conditions of the experiment: initial concentration of MO approx. 4 µg/cm³; pH 6; current density 2.021 mA/cm².

As can be seen from Fig. 6,the total dye removal efficiency was almost the same for decolorization running in the solutions with 4 - 6 g/dm^3 NaCl (decolorization or η = 89 %). Very similar decolorization rate and the total treatment time at higher concentrations of NaCl (<4 g/dm^3) was observed by YUSUF *et al*. (2016), where KCl solution was used as supporting electrolyte (<0.1 M). Efficiency of decolorization was almost the same and small differences were probably caused by different electrode material (polymer electrode).Lower efficiency was obtained in 2 g/dm^3 NaCl solution, where decolorization ratio was only 81.3%.

This difference can be explained by the deficient production of active chlorine due to the low concentration of chlorine ions in the model wastewater. MO degradation treatment time increased with the decreasing concentration of NaCl. These results correspond to the observations other authors (RAJKUMAR *et al.*, 2007; MARTÍNEZ-HUITLE and BRILLAS, 2009).

4. Conclusions

The methylorange (MO) degradation by electrochemical oxidation on two carbon electrodes was analysed in this study. Electrochemical degradation of MO was tested at various operative parameters. Our results demonstrated that concentration of NaCl, time of electrolysis and the applied current density on electrodes played an important role in the efficiency of dye removal from the model wastewater. At different current densities, probably due to the amount of the produced active chlorine, decolorization ratio was the same, and the rate of the production of the active chlorine played the key role in degradation of MO. The presence of NaCl increased the degradation of MO due to a synergic effect of anodic and basal oxidation, which greatly improved the decolorization rate. The obtained results also showed that the efficiency of MO degradation increased along with the concentration of NaCl electrolyte. The results of this work offer an effective alternative method for enhancing degradation of dyes in liquid solutions and wastewaters.

References

ARAUJO, E.G., SANTOS, A.J., SILVA, D.R., SALAZAR, R., MARTÍNEZ-HUITLE C.A.: Cysteic acid-modified glassy carbon electrode for monitoring oxalic acid (OA) concentration during its electrochemical oxidation at Ti/Pt anode. Electroanalysis, 26, 2014, 748-755.

AZAMI, M., BAHRAM, M., NOURI, S., NASERI, A.: A central composite design for the optimization of the removal of the azo dye, methyl orange, from waste water using the Fenton reaction. J. Serb. Chem. Soc., 76, 2011, 1-21.

BONIN, P.M.L., BEJAN, D., SCHUTT, L., HAWARI, J., BUNCE. N.J.: Electrochemical reduction of hexahydro-1,3,5-trinitro-1,3,5-triazine in aqueous solutions. Environ. Sci. Technol., 38, 2004, 1595-1601.

BRILLAS, E., MARTÍNEZ-HUITLE C.A.: A central composite design for the optimization of the removal of the azo dye, methyl orange, from waste water using the Fenton reaction. Appl. Catal. B-Environ., 166-167, 2015, 603-643.

CARTER, K.E., FARRELL, J.: Oxidative destruction of perfluorooctane sulfonate using boron-doped diamond film electrodes. Environ. Sci. Technol., 42, 2008, 6111-6118.

CARVALHO, D.A., BEZERRA ROCHA, J.H, FERNANDES, N.S, DA SILVA, D.R., MARTÍNEZ-HUITLE. C.A.: Application of electrochemical oxidation as alternative for removing methyl green dye from aqueous solutions. Lat. Am. Appl. Res., 41, 2011, 127-133.

CHAPLIN, B.P., SCHRADER, G., FARRELL, J.: Electrochemical oxidation of nitrosodimethylamine with boron-doped diamond film electrodes. Environ. Sci. Technol., 43, 2009, 8302-8310.

DU, L., WU, J., QIN, S., HU, C.:Degradation mechanism of Methyl Orange by electrochemical process on RuO(x)-PdO/Ti electrode. Water Sci. Technol., 43, 2011, 1539-1545.

KAR, A., SMITH, Y.R., SUBRAMANIAN, V.: Improved photocatalytic degradation of textile dye using titanium dioxide nanotubes formed over titanium wires. Environ. Sci. Technol., 43, 2009, 3260-3268.

KONG, Y., YUAN, J., WANG, Z.L.: Application of expanded graphite/attapulgite composite materials as electrode for treatment of textile wastewater. Appl. Clay Sci., 46, 2009, 358-362.

KONG, Y., WANG, Z., WANG, Y., YUAN, J., CHEN, Z.: Degradation of methyl orange in artificial wastewater through electrochemical oxidation using exfoliated graphite electrode. New Carbon Mater., 26, 2011, 459-464.

LI, S., ZHAO, Y., CHUA, J., LI, W., YU, H., LIU, G.: Electrochemical degradation of methyl orange on Pt–Bi/C nanostructured electrode by a square-wave potential method. Electrochim. Acta, 92, 2013, 93-101.

LORIMER, P., MASON, T.J., PLATTES, M., PHULL, S.S., WALTON, D.J.: Degradation of dye effluent. Pure Appl. Chem., 73, 2001, 1957-1968.

MA, H., WANG, B., LUO, X.: Studies on degradation of methyl orange wastewater bycombined electrochemical process. J. Hazard. Mater, 149, 2007, 492-498.

MA, X.J., ZHOU, M.H.: A comparative study on azo dye decolorization by electro-Fenton in two common electrolytes. J. Chem. Technol. Biot., 84, 2009, 1544-1549.

MARTÍNEZ-HUITLE, C.A., BRILLAS E.: Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review. Appl. Catal. Environ.,87, 2009, 105-145.

PANIZZA, M., BARBUCCI, A., DELUCCHI, M., CARPANESE, M.P., GIULIANO, A., CATALDO-HERNANDEZ, M., CERISOLA G.: Electro-Fenton degradation of anionic surfactants. Sep. Purif. Technol., 118, 2013, 394-398.

PANIZZA, M., BOCCA, C., CERISOLA, G.: Electrochemical treatment of wastewater containing polyaromatic organic pollutants. Water Res., 34, 2000, 2601-2605.

RAJKUMAR, D., SONG, B.J., KIM, J.G.: Electrochemical degradation of Reactive Blue 19 in chloride medium for the treatment of textile dyeing wastewater with identification of intermediate compounds. Dyes Pigments, 72, 2007, 1-7.

RAMÍREZ, C., SALDAÑA, A., HERNÁNDEZ, B., ACERO, R., GUERRA, R., GARCIA-SEGURA, S., BRILLAS, E., PERALTA-HERNÁNDEZ, J.M.:

Electrochemical oxidation of methyl orange azo dye at pilot flow plant using BDD technology. J. Ind. Eng. Chem., 19, 2013, 571-579.

SALA, M., GUTIERREZ-BOUZAN, C.M.: Electrochemical techniques in textile processes and wastewater treatment. Int. J. Photoenergy, 9, 2012, 1-8.

SANTOS, E.V., SÁEZ, C., MARTÍNEZ-HUITLE, C.A., CAÑIZARES, P., RODRIGO, M.A.: The role of particle size on the conductive diamond electrochemical oxidation of soil-washing effluent polluted with atrazine. Electrochem. Commun., 55, 2015, 26-29.

SHAKIR, K., ELKAFRAWY, A.F., GHONEIMY, H.F., BEHEIR, S.G.E., REFAAT, M.: Removal of rhodamine B (a basic dye) and thoron (an acidic dye) from dilute aqueous solutions and wastewater simulants by ion flotation. Water Res., 44, 2010, 1449-1453.

SIRÉS, I., CABOT, P.L., CENTELLAS, F., GARRIDO, J.A., RODRÍGUEZ, R.M., ARIAS, C., BRILLAS, E.: Electrochemical degradation of clofibric acid in water by anodic oxidation: Comparative study with platinum and boron-doped diamond electrodes. Electrochim. Acta, 52, 2006, 75-82.

SIRÉS, I., BRILLAS, E., OTURAN. M.A., RODRIGO, M.A., PANIZZA, M.: Electrochemical advanced oxidation processes: today and tomorrow. A review. Environ. Sci. Pollut. R., 21, 2014, 8336-8367.

VALERO, D., ORTIZ, J.M., EXPOSITO, E., MONTIEL, V., ALDAZ, A.: Electrochemical wastewater treatment directly powered by photovoltaic panels: electrooxidation of a Dye-containing wastewater. Environ. Sci. Technol., 44, 2010, 5182-5188.

YUSUF, A.H., REDHA, M.Z., BALDOCK, S.J., FIELDEN, P.R., GODDARD, N.J.: An analytical study of the electrochemical degradation of methyl orange using a novel polymer disk electrode. Microelectron. Eng., 149, 2016, 31-36.

ZHOU, M., SÄRKKÄ, H., SILLANPÄÄ, M.: A comparative experimental study on methyl orange degradation by electrochemical oxidation on BDD and MMO electrodes. Sep. Purif. Technol., 78, 2011, 290-297.