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Decolorization of reactive violet 5 dye in textile wastewater by electrocoagulation

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Abstract

The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals, such as complex components. This study investigates the decolorization of synthetic dye wastewater containing textile dye Reactive Violet 5 (RV5) by electrocoagulation. A laboratory batch reactor was used to investigate the effect of various operating parameters using aluminium (Al), iron (Fe) and stainless steel (SS) anode. The effect of dye concentration, current density, supporting electrolyte, supporting electrolyte concentration, electrolysis duration, and material of anode of the systems were evaluated. Color removal efficiency was 22, 91.5 and 99.8 % in 15 minutes using Al, Fe and SS anode, respectively (j = 10 mA/cm^2, c_{NaCl} = 0.171 M).

Keywords
Electrochemical removal; Reactive dye, RV5

Introduction

Production processes of the textile industry require a huge quantity of water and chemicals, which causes emergence of a huge quantity of wastewater containing acids, bases, dissolved solids, toxic substances and different dyes that present even in small concentrations have to be removed. Traditional methods for the treatment of textile industry wastewater represent a combination of biological, physical and chemical methods [1,2]. Biological treatment of dyeing wastewater is cheaper than other methods, but less efficient in decolorization due to toxicity of wastewater and requires the system of aeration. Although the dyestuff and colored substances in wastewater can be effectively destroyed by an advanced chemical oxidation such as UV/H_2O_2, O_3 [3,4] and adsorption using activated carbon [5,6], the costs of these methods are relatively high for an economically sustainable treatment of the textile industry wastewater. Recently we could note an increased interest in the development of electrochemical methods for removal of toxic organic substances present in wastewater [7-12]. Such methods were also successfully tested in different wastewater containing dye pollutants [13-17].

Nowadays, electrochemical technologies for wastewater processing have reached such a state that they are not only comparable with other technologies in terms of cost, but also are more efficient and more compact. In some situations, electrochemical technologies may be an indispensable step in treating wastewaters containing refractory pollutants [8]. Electrochemical treatment is actually a combination of many processes like anodic oxidation, electrocoagulation and electroflocculation, occurring in the electrochemical reactor. The reactor consists of electrodes (cathodes and anodes), which may be sacrificial or non-sacrificial. Iron and aluminum electrodes are sacrificial electrodes. The use of electrodes depends on electrochemical reactions taking place in the reactor. The desired electrodes for electrocoagulation and electroflocculation are so-called sacrificial electrodes. Non-sacrificial electrodes are appropriate for anodic oxidation.

The aim of this study is to examine electrochemical removal of the textile azo dye Reactive Violet 5 ($C_{20}H_{16}N_3O_{15}S_4$ × 3Na) in aqueous solution using aluminium (Al), iron (Fe) and stainless steel (SS) as electrode material. Reactive Violet 5 (RV5) is a synthetic organic dye whose structural formula is presented in Figure 1. This dye is used as a dye for coloring cotton, wool, silk and polyamide textiles. It is also used in antifreeze.

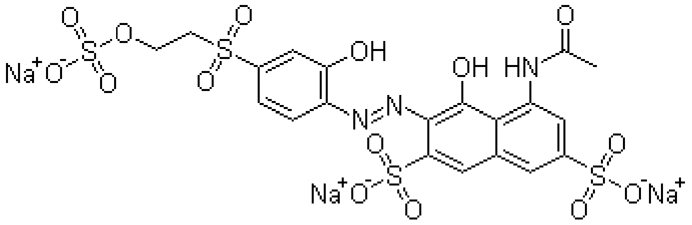

Figure 1. *Structural formula of Reactive Violet 5 dye*

Many microorganisms are capable of azo dyes decolorization, including gram-positive and gram-negative bacteria [15-17] and algae [18,19]. A bacterial consortium RVM 11.1 was selected on the basis of a rapid Reactive Violet 5 dye decolorization. The consortium exhibited 94 % decolorization ability within 37 h under a wide pH range from 6.5 to 8.5 and temperature ranging from 25 to 40 °C. The bacterial consortium was able to grow and decolorize RV5 under static conditions in the presence of glucose and yeast extract and also showed an ability to decolorize in the presence of starch in place of glucose. Maximum decolorization efficiency was observed at 200 ppm (mg/L) concentration of RV5 [17]. Bacterial mixed culture SB4 proved to be proficient in complete decolorization of azo dye - Reactive Violet 5R, which was developed through the culture enrichment technique. SB4 grows well in the minimal medium containing a low amount of glucose and yeast extract (YE) (1 g/L) and the dye of 200 mg/L concentration gets decolorized for RV5 within 18 h under static conditions. Mixed culture SB4 decolorizes a wide range of azo dyes and the maximum rate of decolorization was observed at 37 °C and pH 7.0 [20]. Bioprocess for biodegradation and bioremediation of Reactive Violet 5R (RV5) manufacturing industry's wastewater in the laboratory scale was examined in the designed “down flow fixed film” bioreactor (DFFR), packed with furnace charcoal as a support material. During the batch and continuous operation of DFFR, more than 95 % degradation, 88 % COD reduction and 99 % copper remediation was obtained in less than 8 h of contact time. The continuous mode treatment enables degradation of more than 2500 mg dye in only 1 h of the contact time. The addition of 0.25 % peptone enhanced biodegradation rate by more than three times [21]. Efficiency of the photocatalytic degradation of RV5 by using titanium dioxide was 90 % after 20 min of irradiation and reached nearly 100 % after 80 min under the condition of pH 4 and temperature of 25 °C. Decolorization rate typically followed the first-order reaction, and increased significantly with increasing the amount of photocatalyst, pH, as well as light intensity [22].

Experimental

Commercially available reactive dye, Tecofix Brilliant Violet VS-5R (Reactive Violet 5), from Textilcolor AG, Switzerland, was used in experimental studies. Distilled water was used to prepare the desired concentration of dyestuff solution, and the electrode material used was aluminium (EN 1050; 99.5 %), steel (C.0147; max. 0.08 % C, max. 0.12 % Cr, max. 0.45 % Mn, max. 0.60 % Si) and stainless steel (EN 1.4301/AISI 304). Electrochemical reactor was made of polypropylene (height 95 mm, diameter 71 mm), with the volume of 250 cm^3, at the constant stirring speed (400 rpm) and with the electrodes of the same size placed in it. Both electrodes are made of metal plates (the total effective electrode area was 22.2 cm^2) and the spacing between electrodes was 30 mm. The electrodes were connected to a digital DC power supply (Atten, APS3005SI; 30V, 5A) with potentiostatic or galvanostatic operational options.

All experiments were performed at the constant temperature of 25 °C with 200 cm^3 volume of the wastewater solutions. The current density was adjusted to a desired value and the treatment was started. At the end of electrochemical treatment, the solution was filtered and then analyzed. Before each run, electrodes were washed with 1,1,2-trichloroethene to remove surface grease, and the impurities on the electrode surfaces were removed by dipping for 5 min in a diluted solution of HCl or NaOH.

Total dissolved solids (TDS), pH-value and conductivity were determined according to the Standard Methods for Examination of Water and Wastewater [22]. The pH, conductivity and TDS were measured by a multi meter (Consort C861). The amount of dye RV5 in aqueous solution was measured by using UV-VIS spectrophotometer (Perkin Elmer, Lambda 25), and the IR spectrum was measured by FTIR (Bruker, Tensor 27). Figure 2 and 3 presents adsorption and IR spectra of RV5.

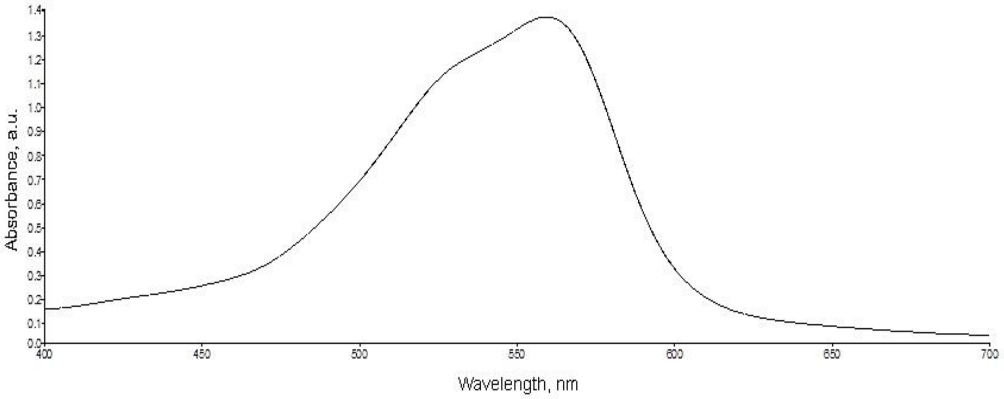

Figure 2. *Adsorption spectra of RV5*

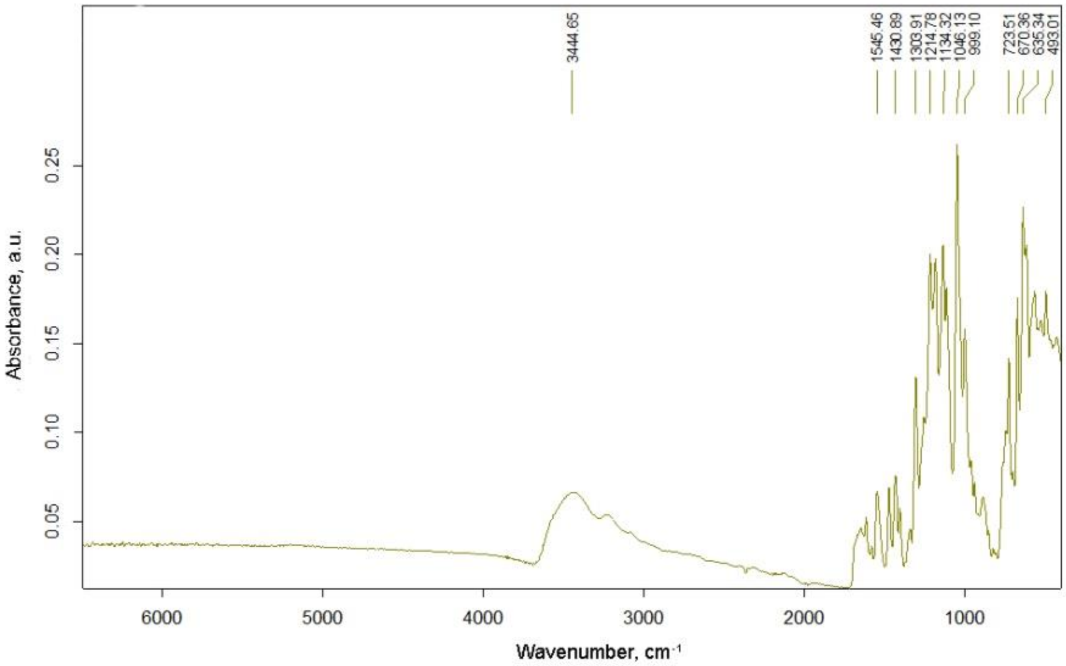

Figure 3. *IR spectra of RV5*

Results and discussion

The aqueous solution of RV5 dye, with the mass concentration γ_{RV5}=100 mg/L, was used for the experimental study of electrochemical removal of organic dyes. The results of electrochemical treatment are expressed through color removal efficiency E_{D} expressed as a percentage and calculated by the following formula:

$$E_{\mathrm{D}} / \% = \frac{\gamma_{\mathrm{i}} - \gamma_{\mathrm{f}}}{\gamma_{\mathrm{i}}} 100 \qquad (1)$$

where γ_{i} and γ_{f} are initial and final dye concentrations expressed in mg/L.

Decolorization efficiency (E_D) was examined in terms of current density, supporting electrolyte, supporting electrolyte concentration, electrolysis time and electrode material in order to determine the optimum operating conditions for maximum decolorization efficiency of the reactive dye. The values of pH, conductivity and TDS of samples are presented in Table 1.

Table 1. *pH values, conductivity and TDS of samples (UZ$_x$)*

Samples	pH	σ, µS cm^{-1}	TDS, mg L^{-1}
UZ$_1$ (100 mg/L RV5)	5.8	123	73
UZ$_2$ (100 mg/L RV5; 0.5 g/L NaCl)	5.8	1084	645
UZ$_3$ (100 mg/L RV5; 1.0 g/L NaCl)	5.8	2030	1210
UZ$_4$ (100 mg/L RV5; 1.5 g/L NaCl)	5.8	2990	1790
UZ$_5$ (100 mg/L RV5; 1.0 g/L Na_2CO_3)	11.2	1767	1056
UZ$_6$ (100 mg/L RV5; 1.0 g/L Na_2SO_4)	5.8	1537	916

Figure 4 presents decolorization efficiency depending on the material of electrodes (anode:cathode) with the presence of the supporting electrolyte (NaCl) of the concentration γ_{NaCl} = 1.0 g/L. Figure 4 presents the effect of choice of electrode material under the same conditions of the treatment, where we notice an advantage of steel (Fe:SS) for decolorization efficiency (>99 %) as anode compared with stainless steel (SS:SS) and aluminium (Al:SS). In all cases cathode is made of stainless steel.

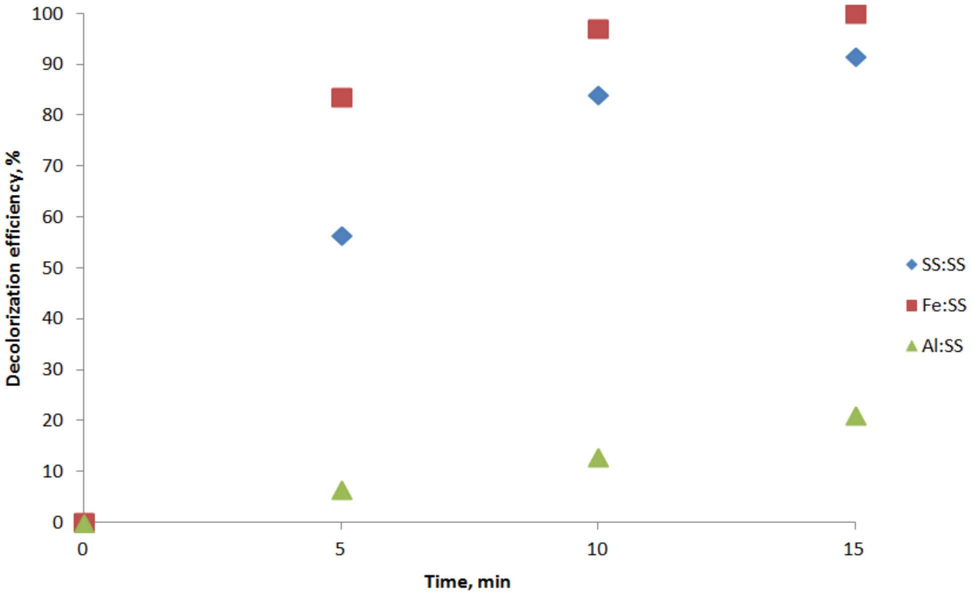

Figure 4. *Effect of electrode material on the efficiency of colour removal* (j = 10 mA/cm^2, γ_{NaCl} = 1 g/L)

Different anode material causes different reaction mechanisms (reaction order). In the case of iron and stainless steel it is a first-order reaction, and the reaction at the anode of aluminum is a zero-order (Figure 5.).

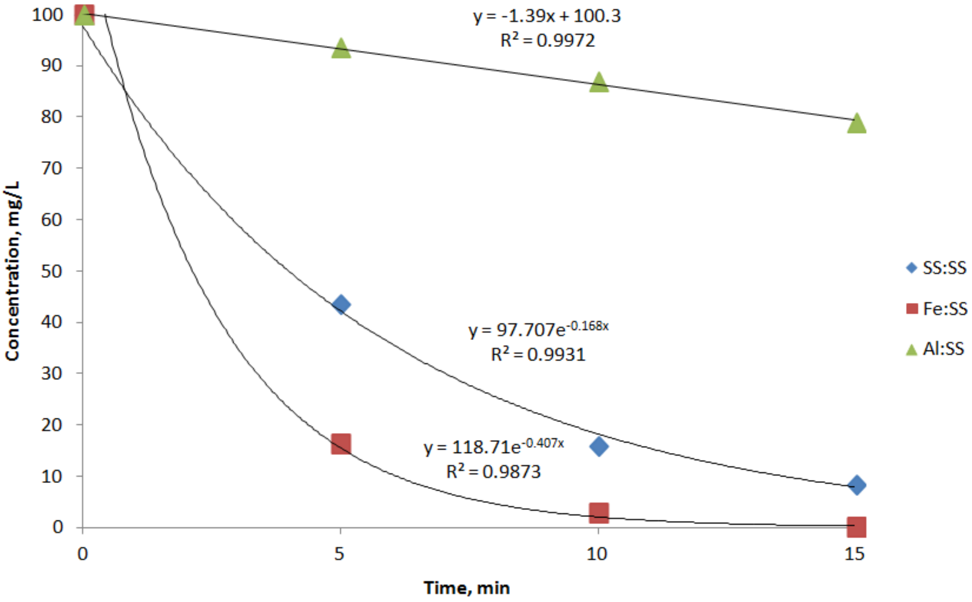

Figure 5. *Effect of concentration (RV5) on time* (j = 10 mA/cm^2, γ_{NaCl} = 1 g/L)

The effect of the supporting electrolyte under the same conditions of the treatment is presented in Figure 6 where we notice a great advantage of NaCl compared with Na_2CO_3 and Na_2SO_4 that have almost identical results.

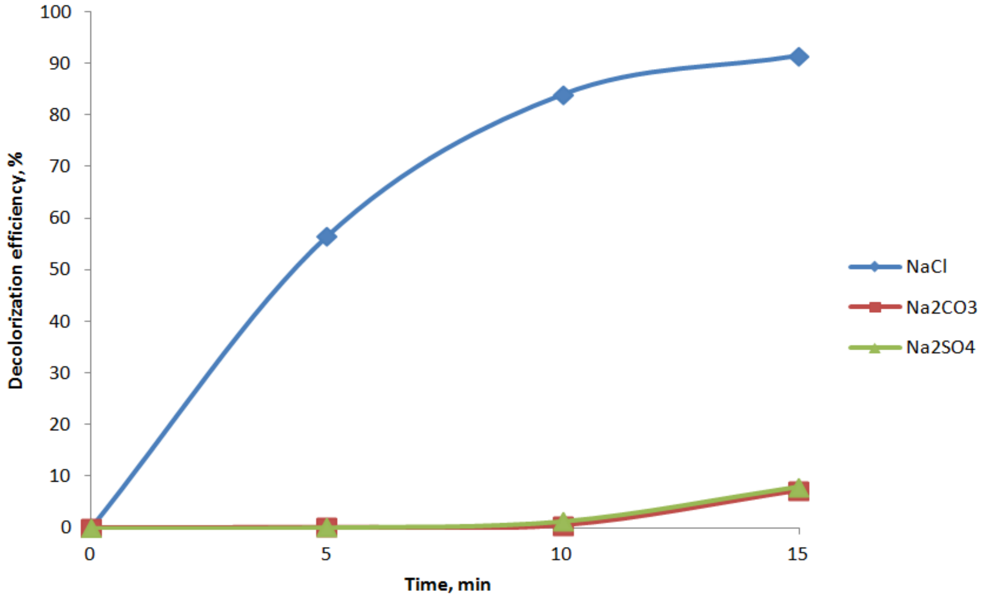

Figure 6. *Effect of supporting electrolyte on the efficiency of colour removal* (j = *10 mA/cm*^{2}, $\gamma_{s.e.}$ *= 1 g/L)*

Decolorization efficiency without the presence of a supporting electrolyte, due to small conductivity and impossibility to apply the currents of higher density, in the above described reactor, is very low (10.5 % in 15 min.), while the efficiency significantly increases (91.5 % for j = 10 A/cm^2, t = 15 min.) with the increased concentration of the supporting electrolyte (NaCl) up to 1 g/L (0,171 mol/L), which represents an optimal concentration of the supporting electrolyte. Values of the concentration above 1 g/L NaCl insignificantly increase decolorization efficiency (Figure 7.).

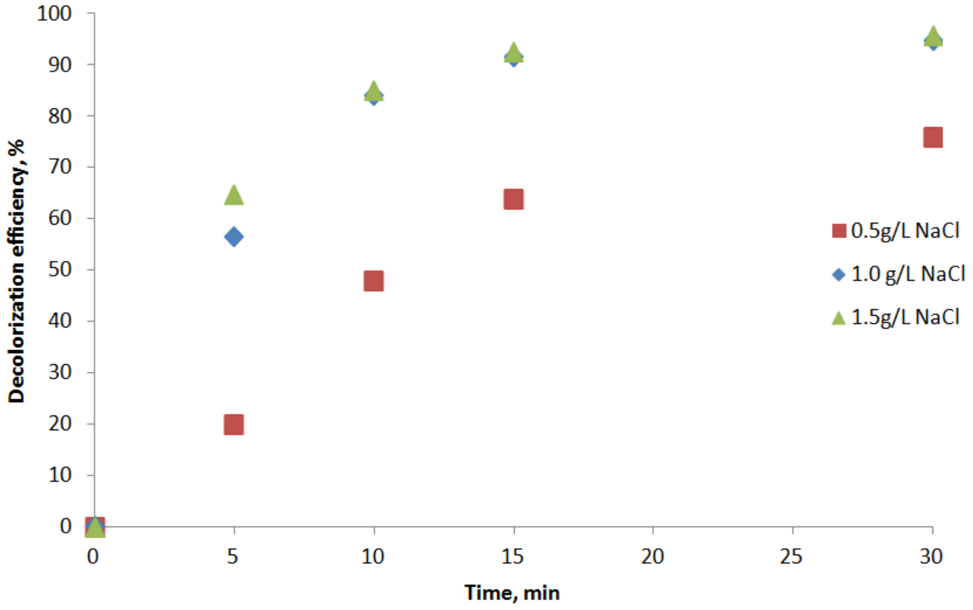

Figure 7. *Effect of concentration of NaCl on the efficiency of colour removal* (j = *10 mA/cm*^{2}*)*

Figure 8 presents increase of decolorization efficiency in 30 minutes of electrolysis depending on the concentration of the supporting electrolyte and time of electrolysis (j = 15 A/cm^2). Maximum efficiency of 95.8 % was realized in the conditions of j = 15 A/cm^2, γ_{NaCl} = 1.5 g/L, and 95.7 % in the conditions of j = 15 A/cm^2, γ_{NaCl} = 1.0 g/L in 30 minutes of electrolysis.

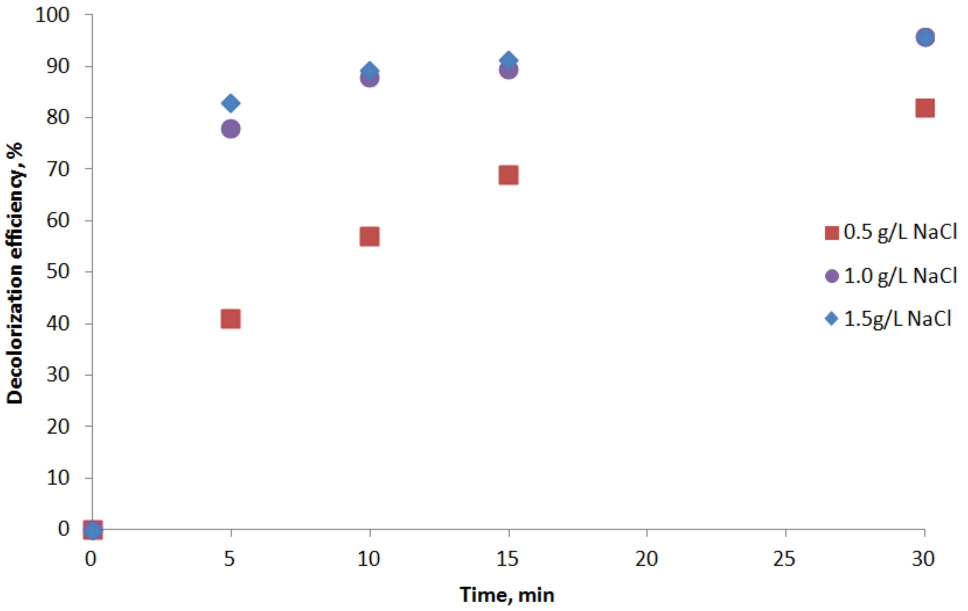

Figure 8. *Effect of concentration of NaCl on the efficiency of colour removal* (j *= 15 mA/cm^2)*

The decolorization efficiency depends on the current density as can be seen the Figure 9. Maximal efficiency of 97 % was reached with the current density j = 25 A/cm^2 in 15 minutes of electrolysis (γ_{NaCl} = 1.5 g/L). Lower values of current density j = 10 A/cm^2 (72 - 92.5 %), j = 15 A/cm^2 (89.5 - 91.5 %) and j = 20 A/cm^2 (92 %) also reached satisfactory values of efficiency. We can conclude from the mentioned values that the optimal current density is j = 10 A/cm^2 with the presence of the supporting electrolyte of the minimal concentration γ_{NaCl} = 1.0 g/L.

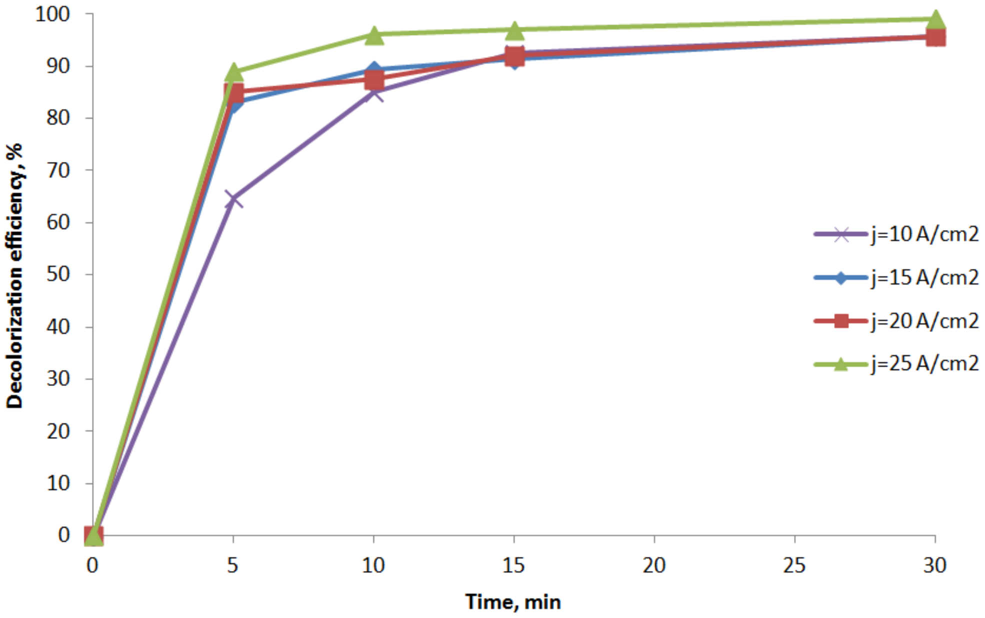

Figure 9. *Effect of current density (10-25 A/cm^2) on the efficiency of colour removal (γ_{NaCl} = 1.5 g/L)*

The time of electrolysis depends on the desired decolorization efficiency. The electrolysis lasting for 5 minutes can achieve the efficiency of up to 89 %, and further increase of time insignificantly increases efficiency for bigger applied current densities, while for smaller current densities (j = 10 A/cm^2) time significantly affects decolorization efficiency. Figure 10 presents adsorption spectra of samples before nad after treatment.

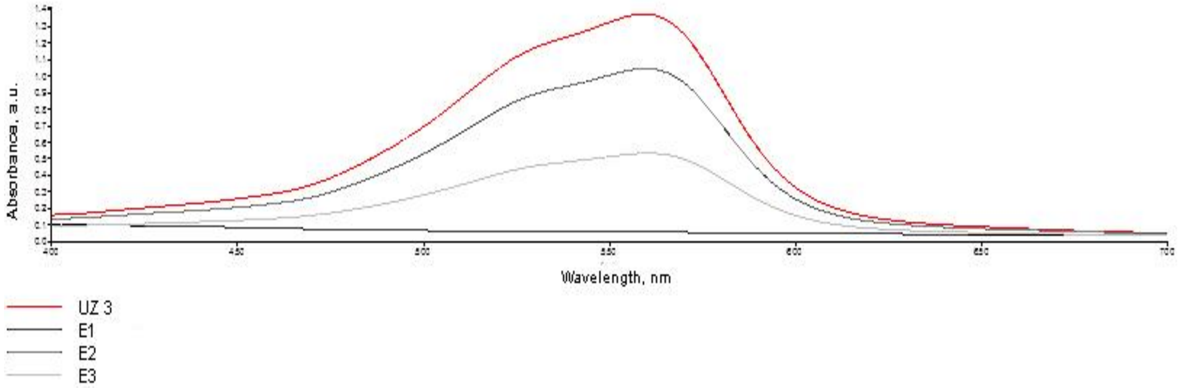

Figure 10. *Adsorption spectra of sample UZ$_3$ (γ_{RV5} = 100 mg/L ,γ_{NaCl} = 1.0 g/L,* j *= 10 A/cm^2) and samples* E$_x$ *after treatment (2,5, 5 and 15 min.) with Fe:SS electrodes*

Conclusions

Electrochemical treatment is one of the most effective techniques to remove color and organic pollutants from wastewater. Decolorization efficiency by this electrochemical process was influenced by current density, supporting electrolyte, supporting electrolyte concentration, electrolysis time and electrode material. The results showed that the supporting electrolyte and electrode material were the most significant parameters. Electrolysis time and current density are important factors if we want to achieve a complete decolorization efficiency. Almost complete removal of dye (99.1 %) was obtained with the following operating conditions, j = 25 A/cm^2, γ_{NaCl}=1.5 g/L, 30 minute operating time in the reactor with the SS:SS electrode combination, and 99.8 % efficiency was obtained with the following operating conditions, j = 10 A/cm^2, γ_{NaCl} = 1.0 g/L, 15 minute operating time in the reactor with the Fe:SS electrode combination.

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References

[1] J. S. Do, M. L. Chen, *J. Appl. Electrochem.* **24** (1994) 785–790.
[2] S. I. Abo-Elela, F. A. El-Gohary, H. L. Ali, R. SH. Abdel-Wahaab, *Environ. Technol.* **9** (1988) 101-108.
[3] G. Chen, L. Lei, P.L. Yue, *Ind. Eng. Chem. Res.* **38** (1999) 1837-1843.
[4] W. Chu, C. W. Ma, *Water Res.* **34** (2000) 3153-3160.
[5] S. H. Lin, C. H. Lai, *Water Res.* **34** (2000) 763-772.
[6] G. Sun, X. Xu, *Ind. Eng. Chem. Res.* **36** (1997) 808-812.
[7] D. Rajkumar, K. Palanivelu, *J. Hazard. Mater.* **B113** (2004) 123-129.
[8] G. Chen, *Sep. Purif. Technol.* **38(1)** (2004) 11-41.
[9] L. Szpyrkowicz, S. N. Kaul, R. N. Neti, S. Satyanarayan, *Water Res.* **39** (2005) 1601-1613.
[10] B. Malinovic, M. G. Pavlovic, S. Bunic, *J. Environ. Prot. Ecol.* **15(4)** (2014) 1574-1582.
[11] M. Kraljić Roković, M. Čubrić, O. Wittine, *J. Electrochem. Sci. Eng.* **4(4)** (2014) 215-225
[12] C. E. Barrera-Díaz, G. Roa-Morales, P. Balderas Hernández, C. M. Fernandez-Marchante, M. A- Rodrigo, *J. Electrochem. Sci. Eng.* **4(4)** (2014) 285-296
[13] S. H. Lin, C.F. Peng, *Water Res.* **28** (1994) 277-876.

[14] A. Gurses, M. Yalcin, C. Dogar, *Waste Manage.* **22** (2002) 491-499.
[15] M. Kobya, O.T. Can, M. Bayramoglu, *J. Hazard. Mater.* **100** (2003) 163-178
[16] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, *J. Hazard. Mater.* **129** (2006) 116-122.
[17] .l Ghernaout, A. I. Al-Ghonamy, M. W. Naceur, N. A. Messaoudene, M. Aichouni, *J. Electrochem. Sci. Eng.* **4(4)** (2014) 271-283
[18] R. K. Sani, U. C. Banerjee, *Microb. Technol.* 24 (1999) 433-437.
[19] K. M. Kodam, I. Soojhawon, P. D. Lohande, K. R. Gawai, *Word J. Microbiol. Biotechnol*. **21** (2005) 367-370.
[20] S. Moosvi, H. Kehaira, D. Madamwar, *World J. Microbiol. Biotechnol*. **21** (2005) 667-672.
[21] D. S. L. Balan, R. T. R. Monteneiro, *J. Biotechnol. 89* (2001) 141-145.
[22] P. Verma, D. Madamwar, *World J. Microbiol. Biotechnol.* **21** (2005) 481-485.
[23] K. Jain, V. Shah, D. Chapla, D. Madamwar, *J. Hazard. Mater.* **30** (2012) 378-386.
[24] N. Sheth, S. Dave, *Bioresource Technol.,* **101** (2010) 8627-8631.
[25] Y. C. Chung, C. Y. Chen, *Environ. Chem. Lett.* **7** (2009) 347-352.
[26] American Public Health Association (APHA), *Standard Methods for Examination of Water and Wastewater*, 17th ed., Washington, DC, 1992.