

Utilization of a new optical sensor unit to monitor the electrochemical elimination of selected dyes in water

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Abstract. This paper presents results obtained by developed optical sensor, which consist from multi-wavelength LED light source and two photodetectors capable of measuring the change in optical signal along two different optical paths (absorbance and reflectance measurements). Arduino microcomputer was used for light source management and optical signal data measuring and recording. Analytical validation of developed optical sensor is presented in this paper. The performance of the system has been tested with varying water solution of dyes (malachite green, methyl orange, trypan red). These results show strong correlations between the optical signal response and colour change from the dyes. Sensor was used for continual in-situ monitoring of electrochemical elimination of selected dyes (current density 15.7 mA cm⁻², electrolyte volume 4 L and NaCl concentration 2 g L⁻¹). Maximum decolorization level varies with each dye. For malachite green was obtain 92,7 % decolorization (25 min); methyl orange 90,8% (8,5 min) and trypan red 84,7% decolorization after 33 min of electrochemical treatment.

1. Introduction

Environmental pollution is a global issue. Synthetic dyes are used in many fields of industry. Textile and printing industries are regarded as the most polluting sectors, due to high discharge volume of dyes-contained wastewater. Dyes are highly soluble and persistent in polluted water, because they have long degradation time in the environment [1]. Pre-treatment has been found important for significant decrease of organic content and colour of dye polluted water. 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 [2,3]. Electrochemical oxidation is the process of oxidizing pollutants on the electrode surface, through the formation of disinfectants such as oxygen species from water itself as in equation (1-5):



If suitable electrolyte is presence in solution (e.g. NaCl), it lead to formation of active chlorine [4] as in equation (6-8):





Even low concentration of chlorides in water ($0,004 \text{ mol L}^{-1}$) is sufficient for electrochemical elimination undesired pollution and production of active chlorine in effective level. This level of chlorides is naturally presence in surface waters [4].

Common used UV/VIS spectrophotometric methods for monitoring of water quality are based on specific absorption of light with various wavelengths [5]. The current trend is to simplify and increase the effectiveness of pollution monitoring in real time. Recent development in optoelectronics allows to constructs a low cost in-situ sensor for continuously monitoring. Optical sensors are based on detection of physical changes of light and can be used for qualitative and quantitative analysis of pollution substances. The low cost components allow to connected sensors into monitoring networks and performed real time, continuous *in situ* water pollution analysis [6].

The aim of paper is to verify the possibility of using a low-cost multi-wavelengths spectrophotometric sensor for monitoring the electrochemical purification of water contaminated with selected dyes. The dyes were selected based on the maximum absorption band, which was in the wavelength range corresponding to the radiation of light source inside spectrophotometric sensor. In natural waters these dyes generate toxicological risk for biological system.

2. Materials and methods

Schematic representation of electrochemical treatment device based on previous work [7] with spectrophotometric unit controlled by microprocessor platform Arduino is shown in the figure. 1.

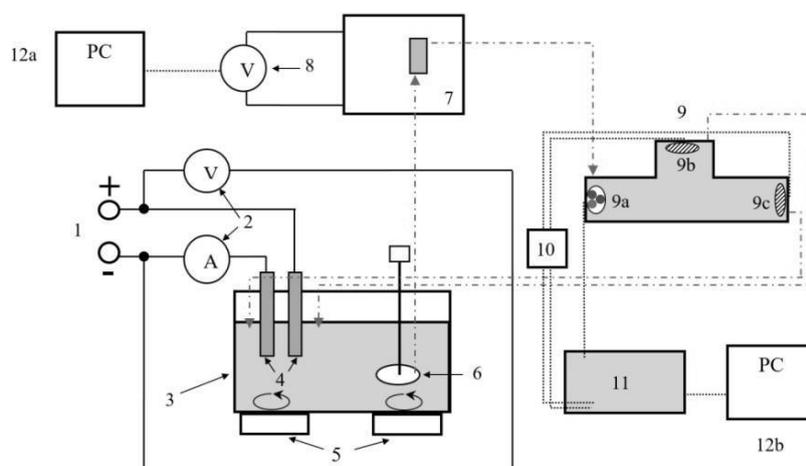


Figure 1. Scheme of the experimental equipment for the electrochemical elimination of dyes in water (1 – DC power supply, 2 – voltmeter and amperemeter with USB, 3 – electrolysis reactor, 4 – carbon electrodes, 5 – magnetic stirrers, 6 – pump, 7 – VIS spectrophotometer with flow cuvette, 8 – voltmeter with USB, 9 - optical sensor unit, 9a – RGB LED light source, 9b – resistance detector of absorbance, 9c – resistance detector of reflection, 10 – A/D converter, 11 - Arduino microcomputer, 12a,b - data logger computers).

The electrolytic cell contained two vertically positioned graphite electrodes (Elektrokarbon, Slovak Republic) connected to a regulated DC power supply (Elektrolyser, Veb Mlw Labortechnik Ilmenau, Germany) and submerged into electrolyte solution (4 L) with 2 g L^{-1} content of NaCl. The resulting electrolyte was used to monitor the process of elimination of selected water-soluble dyes (malachite

green, methyl orange, trypan red). All degradation processes were carried out under the galvanostatic condition at current density $15,7 \text{ mA cm}^{-2}$ at constant laboratory temperature 25°C .

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.

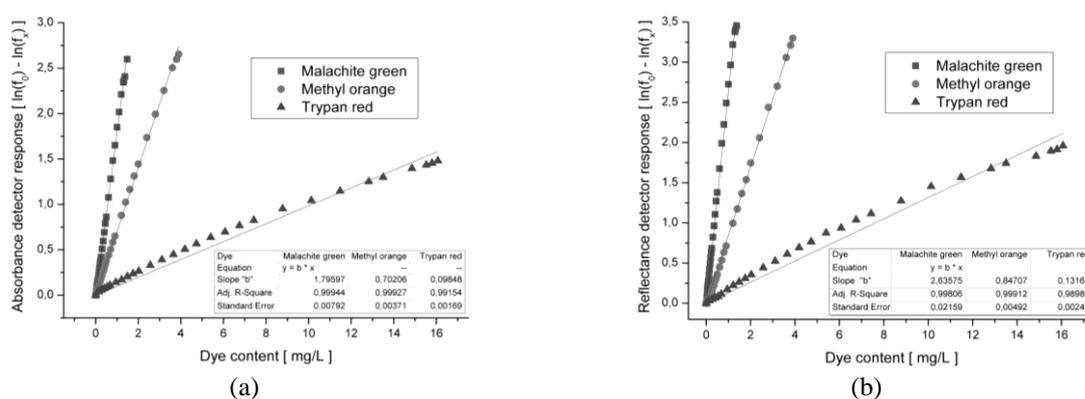
Continual measurement and proper circulations into laboratory spectrophotometer (Spekol 11- Carl Zeiss JENA) in conjunction with measuring cell of spectrophotometric sensor was performed by pumping device. Data from laboratory spectrophotometer was recorded into PC by digital VOLTcraft VC820 with software Digiscop for Windows ver. 2.06. Because output values of spectrophotometer were in electric current, it was necessary to convert these values to absorbance using the calibration curve between these two variables.

The optical sensor is devised to give data on bulk water property changes, particularly opacity and colour changes. For record values gained by spectrophotometric sensor was used the Measurino software with connection to Arduino microcomputer. Detectors in spectrophotometric unit are capable of measuring the transmission of light emitted by RGB LED (Super Flux RGB LED SFL RGB 2200/80° with red LED 620-630 nm, green LED 515-525 nm and blue LED 460-470nm) light source through water, while simultaneously measuring the side-scattering of the light measured at right angles to the transmission path. Arduino measured change in the frequency values on the absorbance photoresistor detector and the reflectance detector (Vactrols VT83N4) after converting via an analog transducer from resistance units.

Elimination efficiency was calculated from ratio of content dye at the initial C_0 and the given C_t time in model waste water. The remaining concentration of dye in wastewater was determined from the equation of the linear dependence between the concentration of dye and absorbance, for solutions with the known concentration of dye.

3. Results and discussion

The results obtained from the laboratory tests on the food dyes are represented here. The accuracy of spectrophotometric sensor response on pollution presence in water can be evaluating against to laboratory spectrophotometer in figure 2c.



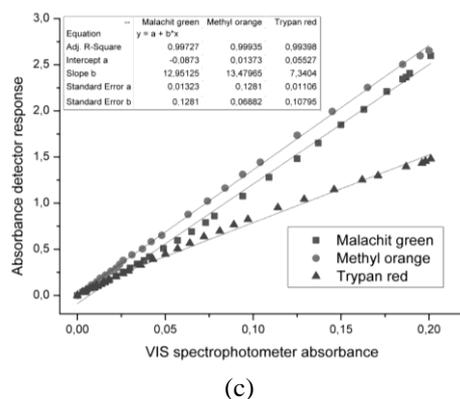


Figure 2. Dependence of absorbance (a) and reflectance (b) detectors response to content of the dyes in water and correlation between the absorbance from VIS spectrophotometer and the absorbance from detector of optical sensor unit (c).

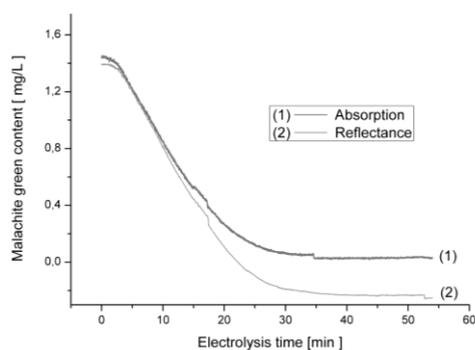
Figure 2 a,b shows the absorbance and reflectance detector response on change in the optical signal caused by increasing concentration of selected dyes in tested water. Response of detector is shown to be a linear, for absorbance detector with $R^2 > 0.99$. Response of reflectance detector was less accuracy due to very low irradiation of photoresistor close to detection limit. Dyes solutions were clear without signs of turbidity. Response recorded by reflectance detector was caused by my measuring reflected light on sensor cover and its absorption by dye. In fact reflectance detector during calibration test measure absorption and trend of calibration curves from absorbance and reflectance detector are very similar.

Table 1. Evaluation of electrochemical elimination of dyes by absorption detector.

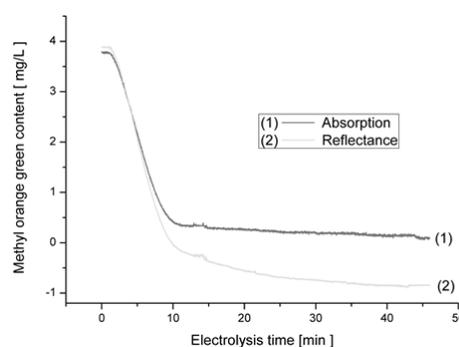
Dye	Initial content (mg/L)	Electrolyses time (min)	Elimination efficiency (%)	Rate constant (min^{-1})		
				Value	Adj. R-Square	St. Err.
Malachite green	1.37	25	92.7	-0.05562	0.97237	2.35E-04
Methyl orange	3.7	8.5	90.8	-0.43209	0.98846	2.09E-03
Trypan red	14.4	33	84.7	-0.40839	0.95231	2.13E-03

Treatment time needed for maximum level of decolorization varied for each dye (see table 1). Methyl orange and malachite green showed good degradability by electrochemical treatment with elimination efficiency $> 90\%$. In case of electrochemical elimination of trypan red was maximum elimination level only 84.7% gained after 33 min. Electrolysis continued after this time, but elimination efficiency showed no increase. Differences in elimination efficiency were probably caused by different initial content of dye in water, because initial concentration was modified on colour change capability of each dye.

Figure 3 showed continuous recording of electrochemical decolorization dyes from absorbance and reflectance detector.



(a)



(b)

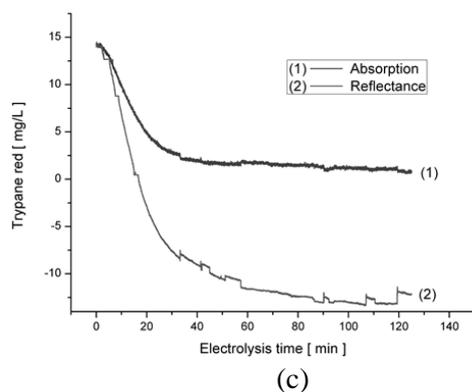


Figure 3. Decrease of content Malachite green (a), Methyl orange (b), Trypan red (c) during the electrolysis, determined by the absorption and reflectance detectors (content NaCl in electrolyte 2 g/L, current density 15,7 mA cm⁻²).

The response of detectors depends on many factors such as light reflection from sensor walls, light source radiation, absorption of radiation by the analyzed substance, radiation of scattering, refractive index. During electrolysis are generated gas bubbles (equations 1-5), which circulate with solution to the sensor measuring cell. Different refractive index of water and air causes increase in light diffusion. This explains the negative absorbance values measured by the reflectance detector, because with treatment time increase saturation of solution, which lead to more irradiation of detector than was measured at the beginning of the experiment. After completion of electrolysis and washing sensor, absorbance measured by at reflectance detector stabilized at the original/blank value. Small deviation observed on both elimination curves for each dyes were cause by attaching gas bubbles nearby detectors and by their removal with temporal increased liquid flow. Response reflectance detector on dispersion confirmed usage for measuring turbidity, which is important fact for next experimental work.

4. Conclusions

Results obtained by developed low cost optical sensor consist from multi-wavelength LED light source and two photodetectors capable for absorbance and reflectance measurements. The performance of the system has been tested with varying water solution of dyes compared with results from laboratory spectrophotometer. These results show strong correlations between the optical signal response changes from the dyes. The results of these experiments suggest, that spectrophotometric unit with new optical sensors can be used to monitoring pollution during electrochemical water treatment.

Acknowledgments

We would like to acknowledge support of this work provided by Department of Ecochemistry and Radioecology, Faculty of Natural Sciences, University of SS Cyril and Methodius in Trnava. This paper was supported by grants FPPV-18-2015 and APVV-14-0716.

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