MONITORING OF CHLORINE BY NEW METHOD BASED ON FOS IN WATER BODIES

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Abstract
Fibre optic sensor (FOS) is used to measure the concentration of total chlorine in samples of surface water, swimming pool water and leachate from MSW landfill. FOS represents new original method which is based on the color of the sample for measurement ofanalyteconcentration. Color sensor converts RGB (Red-Green-Blue) color model to HSV (Hue-Saturation-Value) color model. S and V parameters were used for determination of chlorineconcentrations in selected water bodies. H parameter was used for the calculation of wavelength at which applied sensor measures the concentration of total chlorine. Research was carried out to validate the effectiveness and repeatability of the results obtained with FOS and confirms the capability to use sensor in laboratory controlled conditions. Results obtained with FOS are compared with standard analytical methods (UV-Vis spectrophotometer) to confirm the possibility of using FOS as replacement for standard analytical expensive equipment.

Introduction
Constant contamination of the environment caused by anthropogenic activities requires new improved methods for monitoring of different water bodies. Currently, standard laboratory methods are used for water monitoring, in the absence of better alternatives. They possess certain limiting factors which are related to the use of expensive and specific chemicals, the complexity of the analysis, the loss of the desired analyte in the process of sampling, transportation, extraction and storage. The great disadvantage is impossibility of obtaining *in-situ* and real-time results for the examined water body.

FOS represents inventive equipment for monitoring of aquatic medium. Advantages of FOS compared to the conventional methods are: simple use, low-cost device, small dimensions (which enables measurements where other devices do not have access), resistant to electromagnetic influences and corrosion, enabling measurements in inaccessible and remote areas, possibility to use in high aggressive chemical environments, electric power is not required at sampling points, etc., [1,2,3]. Mentioned advantages allow the use of FOS in the industry, biomedical, civil engineering (construction of dams and buildings), pharmaceutical and many other applications. FOS is used for examination of surface water, groundwater, ocean water, industrial and municipal wastewater, landfill leachate, wastewater from agricultural run-off, acid rain, etc. [4].

In the literature there is a wider range of designed and calibrated FOS that works on different principles. FOS has been developed for measuring of one parameter and as multi-parameter device used for monitoring of the various aqueous solutions. One parameter FOS device were calibrated for measurement of: nitrate [5,6], sodium [7] pH [8], copper [9], potassium [10], BOD (Biological Oxygen Demand) [11]. Multi-parameter sensor devices were designed for measurement of: cyanide, phosphate, sulfate, nitrite, nitrate in aqueous samples [4], metal ions

Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Cd^{2+}, Zn^{2+}, Pb^{2+} and Hg^{2+} in different water bodies [12], measurement of nitrate and ammonium in an aqueous solution [13], prototype field device for measuring organic pollutants in groundwater [14] and orthophosphate, sulfate, nitrite, total chlorine and Cr (VI) in surface water [15].

The aim of this research is to demonstrate the possibility of using laboratory FOS for measurement of chlorine in surface water, swimming pool water and leachate. Chlorine is used for disinfection of drinking water and swimming pool water which are used for recreation and human activities. During disinfection process, toxic and carcinogenic by-products could be generated and could have a negative impact on human health. Contaminated waste water with chlorine compounds could cause pollution of surface and groundwater.

The results obtained by standard analytical methods (UV-Vis spectrophotometer) were compared with the results obtained with the FOS to demonstrate the effectiveness of the sensor and possibility to use for monitoring of various water bodies.

Experimental

Samples of surface water for laboratory analysis were collected from river Danube in the city of Novi Sad, Serbia. Leachate samples were collected from MSW landfill in Zrenjanin, Serbia. Samples of swimming pool water were collected from closed swimming pool in Novi Sad, Serbia. Surface water samples were poured into 1 L plastic bottles, while the samples of leachate and swimming pool water were poured into 1 L glass bottles. All samples were stored in hand refrigerator at 4 ^{0}C, and transported to the laboratory. Analyses were carried out in accredited Laboratory for monitoring of landfills, wastewater and air, Department of Environmental Engineering and Occupational Safety and Health in Novi Sad.

Concentrations of total chlorine in samples were analyzed according to the HACH Method (HACH Method 8167) and measured with UV-VIS spectrophotometer (DR 5000, HACH, Germany).

Operating principle of implemented FOS is the absorption of light. When the light passes through a liquid, certain wavelengths will be transmitted while others are absorbed depending on the color of the tested liquid. Fiber optic sensor detects the color and converts RGB color model in HSV color model. The used sensor determines V and S value and calculates concentration of the parameters of interest, and H value which is used for calculation of wavelength.

The sensor consists of three plastic optical fibres (POFs) that emit red, green and blue components mounted around a central optical fibre collecting light reflected from the mirror. The mirror is located on the underside of the sensor where the optical fiber is compiled. Three light-emitting diodes red, green and blue are set to different frequencies. In this way, detection of the reflected signal is achieved with only one photodetector and three bandpass filters.

Results and discussion

Total chlorine was measured in surface water, closed swimming pool water and leachate by new original FOS method. Results measuredwith FOS were compared with results obtained by standard laboratory methods (UV-Vis spectrophotometer) to demonstrateeffectiveness of applied sensor.

The FOS is calibrated with 4-5 different standard solutions with known concentrations, prepared by diluting standard solution fortotal chlorine. Reference sample with the lowest concentration of residual chlorine have bright pink color and with increasing concentrations of total chlorine, the color of the sample becomes more intense.

FOS converts RGB color model to HSV color model and measure concentration of selected parameter based on color intensity of the sample. Total chlorine concentrations were calculated and determined on the basis of the parameter S, based on calibration curves

obtained with the referent sample. The V value for total chlorine is constant and it is not possible to determine concentrations based on V values with the applied sensor.
Concentrations of total chlorine in Danube river are extremely low and surface water samples were spiked with known concentrations of standard solutions, since the FOS shows some dissipation with lower concentrations. In Table 1are presented the relative differences between total chlorine concentrations measured by UV-Vis spectrophotometer and by FOS in different water bodies.

Table 1. Comparison of total chlorine concentrations obtained by UV-VIS and by FOS forsamples of surface water, swimming pool water and leachate

Samples	UV-Vis [mg/l]	FOS [mg/l]	Relative difference[%]
Surface water	0,165	0,171	3,62
Swimming pool water	0,59	0,562	4,75
Landfill leachate	0.07	1.955	>100%

Based on obtained results, it was determined that FOS can be effectively used to measure the total chlorine concentrations in surface water and swimming pool water. FOS can't be used for determination of total chlorine in leachate from MSW landfill. The influence of matrix, coloration, turbidity, unwanted reactions and high contamination ofleachate samples do not permit use of FOS for this type of water. Removing the color without loss of analyte of interest will allow the use of FOS for wastewater samples.Deviations less than 10% are acceptable and demonstrate the ability to use sensors for monitoringof surface water and swimming pool water.

Conclusion

The further research will be focused on expanding the range of examined parameters. Selection of quality construction components will improve the precision and accuracy of the laboratory device. Increasing the sensitivity of FOS would ensure measurement of low concentrations of selected parameters. FOS is capable to monitor the quality of surface water and especially water from swimming pool.Construction of field device with improved performances will provide higher quality monitoring program and more reliable results which is important in the case of contamination and early responses in order to prevent the contamination of water bodies.

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