Development of an Analytical Method for the Analysis of Industrial Wastewater Effluents

[Agneša Szarka, Svetlana Hrouzková]

Abstract— **A simple and rapid method has been developed using liquid–liquid extraction coupled with gas chromatography–mass spectrometry to extract and determine the organic pollutants in industrial wastewater effluents and treated water samples. Parameters affecting the liquid – liquid extraction performance, such as solvent selection and volume of the sample and the extractive solvent, were studied. Parameters for separation and detection of contaminants were adopted. The developed method was used for the determination of the pollutants in treated industrial water samples.**

Keywords— **industrial wastewater, , liquid – liquid extraction, GC-MS**

I. Introduction

Industrial wastewater effluents represent very complex matrices for the analyses, several components from the matrix can be coextracted with the target compound and interfere in the detection. Because of the complexity of this type of matrices, the first step in the analytical methods used for the identification of the pollutants and controlling the removing of these pollutants during the treatment processes, is the extraction step before the chromatographic analysis. This part of the analytical process has a major impact on the overall process time and the quality of the obtained results. An ideal pretreatment technique should isolate the analytes from the matrix, then clean-up the extract, as well as concentrate the analytes in one step [1]. The most frequently used sample preparation technique for industrial wastewaters are traditional extraction techniques, such as liquid-liquid extraction (LLE) and solid phase extraction (SPE).

The two special essential requirements of industrial wastewater effluents analysis are the following: high sensitivity and high performance to separate multicomponent samples. The final phase of the analytical method is the identification and determination of analytes using an appropriate instrumental technique. The commonly used methods for the determination of complex organic pollutants are gas chromatography (GC) and liquid chromatography (LC) in combination with mass spectrometry (MS) or tandem mass spectrometry (MS/MS).

Industrial wastewater effluent undergoes a series of treatment steps before it is disposed into the aquatic environment [2]. Treatment technologies concerning electrochemical methods are shown to be time and operation efficient as well as cost-effective. However, sensitive analytical procedures are needed for controlling the occurrence of organic pollutants in treated wastewater samples before discharging into the environment.

This research is focused on development of an analytical method for the determination of organic pollutants in industrial wastewater effluents and electrochemically treated wastewater samples. The optimization of the extraction procedure based on liquid-liquid extraction (LLE) is the first task followed by adaptation of experimental parameters for optimal separation and detection of pollutants from paint industry effluent samples by gas chromatography-mass spectrometry (GC-MS). Next, the selection of key purity markers in original and treated water effluents is the main objective.

II. Experimental part

Industrial water effluents were obtained from the paint industry Slovlak Košeca, a.s. Industrial wastewater treatment was carried out by Hofitech, s.r.o. All samples were extracted by LLE prior to analysis, which was used to isolate contaminants (markers of interest) from samples. The extracts were subsequently analyzed by gas chromatography (Agilent 7890N) with mass spectrometry detection (Agilent 5975). The analytes were separated on a CP-Sil 8 CB capillary column (Agilent Technologies), 15 m × 0.15 mm I.D. × 0.15 μm film thickness. The mass spectrometer was operated in electron ionization mode (70 eV). For a full scan (FS), the mass range of 40-550 m/z was selected. In selected ion monitoring (SIM) mode, ions were sorted into groups; the dwell time used was 10 ms.

III. Results and Discussion

LLE has shown to be an effective technique for the isolation of pollutants from industrial water effluents. The selection of an appropriate extraction solvent was essential for the development of an effective LLE procedure because the physical properties of a specific solvent determine the ability to extract targeted analytes. Four organic solvents with different polarity namely toluene, hexane, dichloromethane, and acetonitrile were tested. The phase separation was satisfactory unless in the case of acetonitrile, therefore, the addition of 1 g NaCl to salt-out the phases was needed. It can be seen in Figure 1, that the highest peak areas for most of the analytes were obtained for toluene as an extraction solvent.

Subsequently, different ratios of sample volume to extraction solvent volume were tested. The ratio of 5 ml sample to 5 ml solvent and 8 ml sample to 3 ml solvent was tested, and the extraction efficiency was compared using toluene and hexane as extraction solvents. For both extraction solvents, higher peak areas were obtained using 3 mL of

solvent for the extraction of the pollutants from 8 mL of industrial water samples. Finally, for further experiments, 3 mL of toluene was used as the extraction solvent.
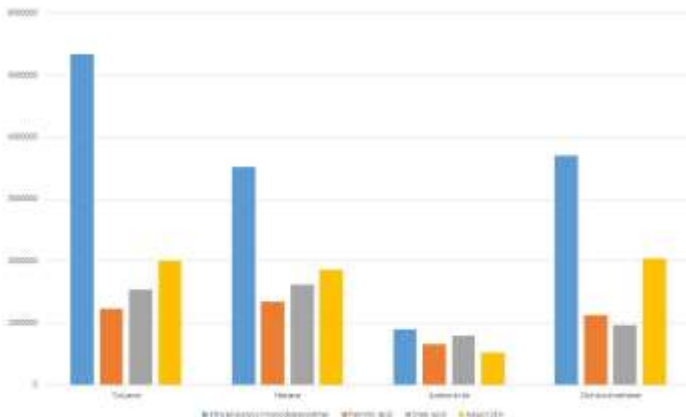

Figure 1. Selection of extractants for LLE

Effective separation of pollutants from industrial wastewater extracts was obtained by GC-MS using non-polar stationary phase employing programmable-temperature vaporization injection. GC-MS in FS mode was applied to identify the organic pollutants contained in the sample. Identification was performed by comparing mass spectra with NIST library data. Totally 17 compounds were identified in the sample extract. Identification of five compounds was confirmed by the analysis of reference materials and these analytes were selected as markers for further studies. The list of the selected markers can be seen in Table 1.

Table 1: List of the identified markers, their chemical formula and molecular mass

Analytes	Chemical formula	Relative molecular mass
Ethylene glycol monododecylether	$CH_3(CH_2)_{11}OCH_2CH_2OH$	230.39
Palmitic acid	$C_{16}H_{32}O_2$	256.42
Oleic acid	$C_{18}H_{34}O_2$	282.47
Adipol 2EH	$C_{22}H_{42}O_4$	370.6
Diethylene glycol dibenzoate	$(C_6H_5CO_2CH_2CH_2)_2O$	314.33

The developed analytical method was applied for the analysis of the treated industrial water samples. Industrial water effluent was treated at different test setups. Constant electrical parameters were used in all cases, two different treatment times and two various additives (organic and inorganic) were tested. The optimized LLE method was used to isolate the analytes from purified water samples, and the extracts were subsequently analyzed by GC-MS in SIM mode. The peak areas of the five identified pollutants in treated water samples were recorded. The chromatograms of the treated samples showed partial or complete removal of most compounds in studied treatment systems.

IV. Conclusion

The study was focused on the selection of the suitable LLE extraction parameters for the isolation of various types of contaminants from industrial wastewater effluents. Samples of industrial waste water effluents were analyzed by LLE-GC-MS method and the occurrence of the organic pollutants were searched. For the treatment procedures, a new ecological technology based on the application of electro-thermochemical technology was used for removing the organic pollutants in industrial water. Finally, the developed GC-MS method with optimized LLE preconcentration step was successfully applied to the analysis of the treated water samples.

Acknowledgment

References

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