



GC–MS methods for the evaluation of the performance of electrochemical water treatment for the degradation of pollutants from paint industry effluents

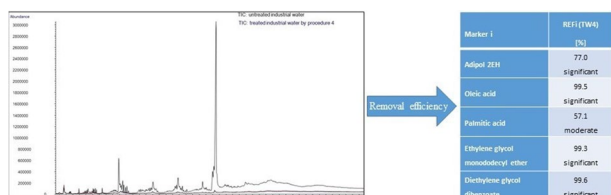
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Abstract

Global production of paint generates a large volume of waste which affects human health and creates an environmental burden. The purpose of this study has been the evaluation of the performance and the control of the efficiency of a hybrid electro-thermochemical wastewater treatment technology able to transform dissolved pollutants into metal oxide/carbide powders and to produce water ready to be reused in manufacturing cycles. In this study, simple and fast method based on liquid–liquid extraction combined with gas chromatography–mass spectrometry has been proposed for the identification of environmental pollutants in industrial water effluents. Parameters affecting the liquid–liquid extraction efficiency were thoroughly studied to ensure high accuracy and precision of the method. The proposed method was successfully applied to the identification and determination of markers levels in a comparison study between the original and treated water effluents. Removal efficiency factors were defined and the power of removal was discussed in terms of weak, moderate, and significant markers removal. The evaluation showed significant removal of markers in water treatment processes employing various additives.

Graphical abstract



Keywords Ecology · Extraction · Gas chromatography · Industrial water · Pollutants · Water treatment

Introduction

The development of modern industrialization and economic globalization produce high volume of industrial wastewater discharge, which causes a formidable global environmental problem [1]. Industrial wastewater such as sewage sludge, livestock manure, food waste, agricultural wastes, and pulp waste is one of the major sources of water pollution [2, 3]. The water discharge from the industrial activities without previous treatment contains contaminants and pollutants which can generate several negative effects on the human and environment [2]. A very big imbalance in the ecosystem

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should be posed by the disposal of highly contaminated effluents due to their harmful effects on aquatic life, human beings, and animals [3]. Therefore, industrial wastewater treatment is an essential and at the same time a very challenging task, because of its complex composition and varying characteristics [4]. Industrial wastewater effluent undergoes a series of treatment steps before it is disposed into the aquatic environment, which include applications of several physicals, chemical, and biological methods [5].

The paint industry is one of the main contributors to contaminating the soil and water resources [6]. It was shown that the major components of the paint industrial wastewater effluent are sourced from the cleaning of equipment and various other unit operations used during the production [7]. Therefore, adequately treated water could be effectively recycled and reused in the production as a coolant, dilutant, or component of low-cost paint and for efficient water management [8].

Plenty of treatment processes have been used up till now such as oxidation, adsorption, sedimentation, chemical precipitation, and biological processes [9]. These treatment methods are not attractive as they are not cost-effective, proceed slowly, and require temperature and pressure control. Their biggest drawback is that they do not completely eradicate the toxic pollutants. However, they convert these pollutants to less-toxic products needing further elimination [10]. Recently, electrochemical methods started to be used for the wastewater treatment. Technologies concerning electrochemical methods are shown to be time and operation-efficient as well as cost-effective [11]. Furthermore, electrochemical methods have numerous advantages such as low sludge production, simple equipment, no chemical additives, and faster settling of flocs produced during operation [12, 13]. However, compared to other wastewater treatment processes, only a few studies have been done on electrochemical treatment.

Some methods have been developed for screening pollutants in industrial water effluents by using gas chromatography in combination with mass spectrometry (GC–MS) [14–16] but several studies were published using gas chromatography–tandem mass spectrometry (GC–MS/MS) [17]. For the isolation and preconcentration of the pollutants, a proper sample preparation technique is required. Mainly traditional extraction techniques have been used for this purpose, such as liquid–liquid extraction (LLE) [14] and solid phase extraction (SPE) [16, 18]. In recent years, microextraction techniques, such as dispersive liquid–liquid microextraction (DLLME) [15] have started to be used.

This paper is focused on the evaluation of industrial wastewater from the paint industry and the control of the electro-thermochemical treatment processes that transform wastewater into clean water and its organic and inorganic content into micro powders with significant reduction of

water toxicity and an increase of cost-efficiency compared with competing technologies. The removal efficiency of the treatment method is discussed in terms of the removal efficiency factors (REFi). Simple and fast method based on LLE combined with GC–MS is proposed for the identification of pollutants in paint industry effluent samples. Next, the identification of key purity markers determination in original and treated water effluents was the main objective.

Results and discussion

Many different types of paints and covering materials are produced by paint manufacturers, containing organic solvent-based and water-based paints, respectively. Both types of production generate waste with negative effect on the environment, which is against the concept of sustainability. There are many significant waste streams generated by paint manufacturing but the largest contribution (80%) is from equipment cleaning [18]. To prevent product contamination and restore operational efficiency, the process equipment is routinely cleaned. Since paint manufacturing is not a chemical conversion operation but a blending operation, the input materials are presented compounds in the wastes [19].

The four main components of paint are resin, additives, solvents, and pigments. These components have different physicochemical properties; therefore, different methods must be used for the isolation of these pollutants from the industrial water samples.

The sample of the wastewater effluent from Slovák Košeca, a.s. is mainly a result of water used to wash the tanks, pipes, and filling machines used to produce and package the products. The products are produced in batches, with different technology procedures scheduled in the same vessels. When changing the product, vessels must be thoroughly cleaned. The wastewater effluent is made up of diluted paint. In this study, LLE was used for the isolation of pollutants and the effluents followed by fast GC–MS.

Evaluation of the LLE method

LLE method was used as the first step for the extraction of pollutants from industrial water samples. The selection of a suitable extraction solvent is the most important step for the establishment of an effective LLE method. Extraction solvents with different polarity (toluene, hexane, dichloromethane, and acetonitrile) were investigated for the isolation of the pollutants. The optimal extraction solvent has to extract the analyte with high extraction efficiency, it should have low solubility in water, and good chromatographic behavior (chromatogram without interfering peaks and compatible with the chromatographic system). To select the optimal solvent 5 cm³ industrial water sample were vortexed 20 min

with 5 cm³ of the above-mentioned extractive solvents. The phase separation was satisfactory except for acetonitrile, where, the addition of 1 g NaCl to salt-out the phases was needed. The extractions were performed in triplicate and the final extracts were analyzed by GC–MS. To evaluate the extraction efficiency, the peak areas of the selected analytes were compared. The highest peak areas for most of the analytes were obtained for toluene as an extraction solvent.

The optimal ratio of the sample volume and extraction solvent volume was tested as the next step of method development. The ratios sample: toluene (V:V; cm³:cm³), 5:5, 8:3, 8:2, 9:2, and 9:1 were studied in order to obtain optimal ratio for high enrichment of contaminants in the extract as well as for fast and easy manipulation with extract withdrawal. In the case of low extraction solvent volumes such as 2 cm³, a low volume of extract was obtained, and the manipulation during the removing of the extract was complicated. In the case of the ratio 9:1, a cloudy extract solution was formed and the phase separation was not satisfactory for further manipulation. The peak areas of the analytes were higher when 8 cm³ or 9 cm³ of industrial water was extracted by 3 cm³, 2 cm³ of toluene, respectively, in comparison to the ratio 5:5 (cm³:cm³). The analysis of the extracts obtained

using the ratios 8:2, and 8:3 have shown that there was no significant difference in peak areas of the selected markers (Fig. 1), but in case of the ratio 9:2 the peak areas of the studied markers were decreased. It should be explained by the worse phase separation. Therefore, the ratio 8:3 was selected, because the manipulation with the extracts was the easiest out of all mentioned versions, and also a transparent extract was obtained. Re-extraction with toluene showed that a single extraction with 3 cm³ is exhaustive.

Identification of the pollutants in LLE extract

The results of the GC–MS analysis of the industrial water extracts are presented in Table 1. The LLE extracts were analyzed by GC–MS in full scan mode and 17 components were identified by the NIST library. We accepted that organic compounds were present when the probability of the library match was above 90%. The identity of five of the 17 compounds was confirmed by the analysis of reference materials and these analytes were selected as markers for further studies. Table 1 contains the five identified compounds, their retention times, monitored ions, and the probability of the library match. The extracted ion chromatogram

Fig. 1 Comparison of the peak areas of selected compounds with different sample volume: solvent volume ratio for LLE

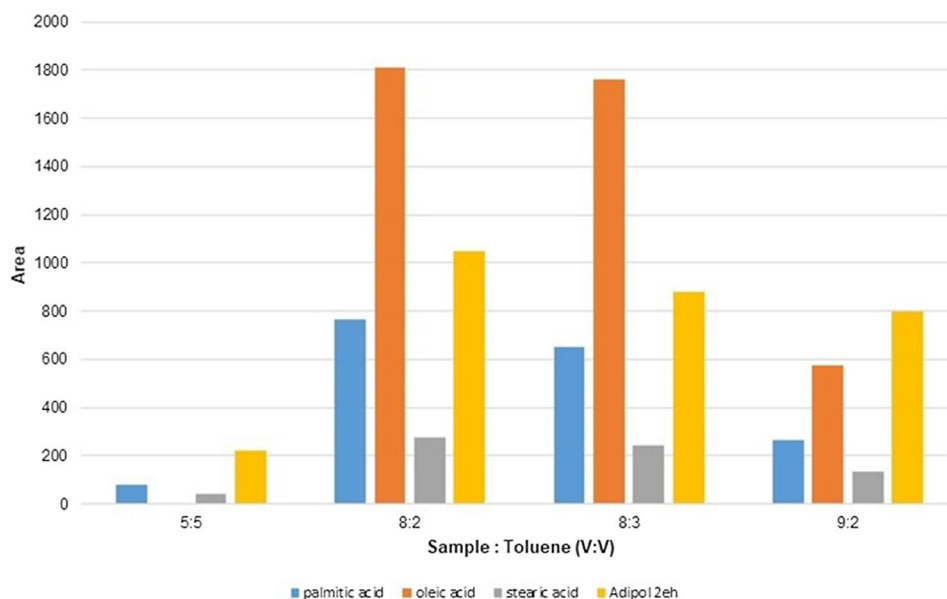


Table 1 List of the identified compounds in industrial wastewater and GC–MS parameters (retention time, monitored ions, and identification parameters)

Analytes	Retention time / min	Monitored ions <i>m/z</i>			CAS no	Library match/%
Ethylene glycol monododecyl ether	4.990	140	111	97	4536-30-5	96
Palmitic acid	6.008	256	213	129	57-10-3	92
Oleic acid	6.677	264	111	95	112-80-1	91
Adipol 2EH	7.500	129	147	112	70147-21-6	97
Diethylene glycol dibenzoate	7.922	149	105	77	120-55-8	96

of the selected markers in industrial water extract is shown in Fig. 2, where a large chromatographic peak of diethylene glycol dibenzoate can be observed.

Glycols and glycol ethers are present mostly in water-based paints. For dyes, resins, lacquers, varnishes, wood stains, and inks ethylene glycols and their derivatives are mostly used as solvents in the industrial sector. Some studies on the determination of volatile organic compounds (VOC) in architectural coatings showed a high concentration of ethylene glycol (EG) (91.2%), propylene glycol (PG), ethylene glycol butyl ether (EGBE), diethylene glycol butyl ether (DGBE) [20]. Glycol ethers, which are generally detected in water-based paints, are reported to cause reproductive damage in males and females. It was reported by recent scientific studies that exposure to fumes from water-based paints could cause asthma, allergies, and eczema in children [20].

The properties of alkyd resins are changed by monobasic acids by controlling functionality, and thus polymer growth, as well as by the nature of their original physical and chemical properties. Most of the monobasic acids, which are used in alkyd resins, are derived from natural glyceride oils and are in different degrees of unsaturation. The most common fatty acids present in these oils include lauric, palmitic, stearic, oleic, linoleic, linolenic, ricinoleic, and licanic acids [21]. Emulsifying agents, formed by the reaction of morpholine with fatty acids in the case of oleic acids used in waxes and polishes, are applied in the formulation of water-resistant waxes and polishes. As the film of polish emulsion

gradually dries, morpholine evaporates to form a film highly resistant to water spotting and deterioration.

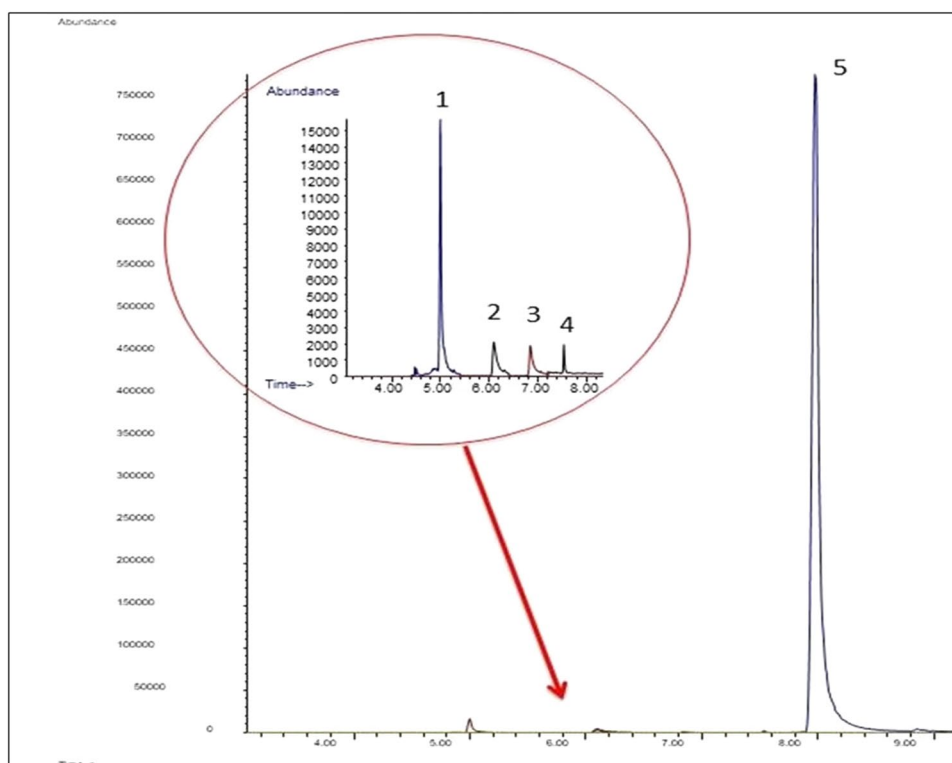
Adipates, like Adipol 2EH, are plasticizers used to improve the elasticity or processability of materials like plastic. Furthermore, they are used in non-PVC applications such as paints, lacquers, and cosmetics. Adipol 2EH is a liver carcinogen in mice and induces developmental toxicity in rat offspring, causing a permanent decrease in body weight [22, 23]. Figure 3 represents the confirmation of Adipol 2EH in industrial water samples, by the analysis of the reference material of Adipol 2EH.

Industrial water treatment

Hofitech is a company that has developed a wastewater treatment technology that is based on electrochemical dissolving of certain metal consumables in the wastewater and the ability of activated metal nanoparticles to chemically capture carbonized or organic impurities found in the wastewater. The metalized semi-organic metaproducts are further processed to metal oxide and metal carbide particles. This technology allows to reduce and transform carbon footprint to zero-carbon materials, i.e. carbides that are harmless and are widely used in industry.

In the verification test, the industrial water effluent was treated using four different test setups. The experiment aimed to select and demonstrate an effect of primary and

Fig. 2 Extracted ion chromatogram of the selected markers in industrial water extract (LLE with 3 cm³ of toluene); 1–ethylene glycol monododecyl ether, 2–palmitic acid, 3–oleic acid, 4–Adipol 2EH, 5–diethylene glycol dibenzoate



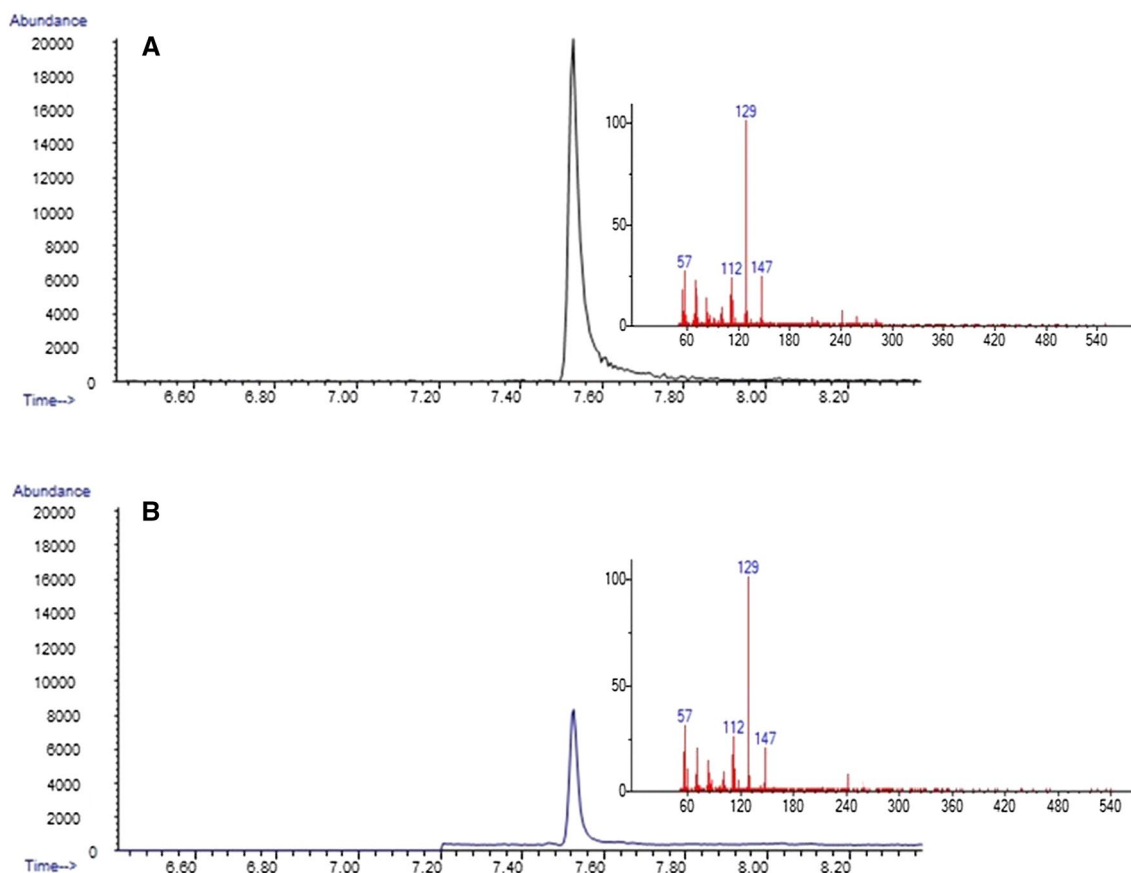


Fig. 3 Extracted ion chromatogram of the standard solution Adipol 2EH (at 2 ng mm⁻³ concentration level) and its EI spectrum (**A**) and of the LLE extract of industrial water samples and its EI spectrum (**B**)

secondary boundary conditions. The samples were considered and tested with two different additives:

- Samples 1 and 2 were treated with an organic additive
- Samples 3 and 4 were treated by an inorganic additive

Both additives were used at two different treatment times and with the same electrical parameters.

Study of markers removal efficiency

Industrial wastewater has a very complex matrix composition because it contains a variety of pollutants at different concentrations. The concentration of these pollutants may fluctuate from very low to very high. Hence, the simultaneous removal of pollutants from such complex industrial wastewater is highly challenging. To determine the treatment efficiency of the four different methods, the LLE extracts of the treated industrial water were analyzed by GC-MS in SIM mode and the peak areas of the five identified and selected markers were compared. The chromatograms of the treated samples showed partial or complete removal of most

compounds in four studied treatment systems. For evaluation, the removal efficiency factor (REF_i) was defined as follows:

$$REF_i = \left(1 - \frac{A(M_i, TW)}{A(M_i, IW)} \right) \cdot 100\%$$

where $A(M_i, TW)$ is the peak area of selected marker i from the extract of the treated water sample, $A(M_i, IW)$ is the peak area of selected marker i from the extract of the untreated industrial water sample.

The removal of selected markers was evaluated as weak if REF_i was in the range of 0% to 30%, moderate if REF_i was in the range of 30–70%, and significant if the REF_i was higher than 70%. Removal efficiency factors for all selected markers for four various treatment procedures are summarized in Table 2.

Diethylene glycol dibenzoate was the most abundant compound in untreated industrial water (Fig. 2). During the treatment process, its amount was significantly eliminated. In the case of inorganic salt addition (treatment 3 and 4), significant removal was obtained, while by the

Table 2 Removal efficiency factors (REF_i) for selected markers for four water treatment technology procedures and the evaluation of markers removal

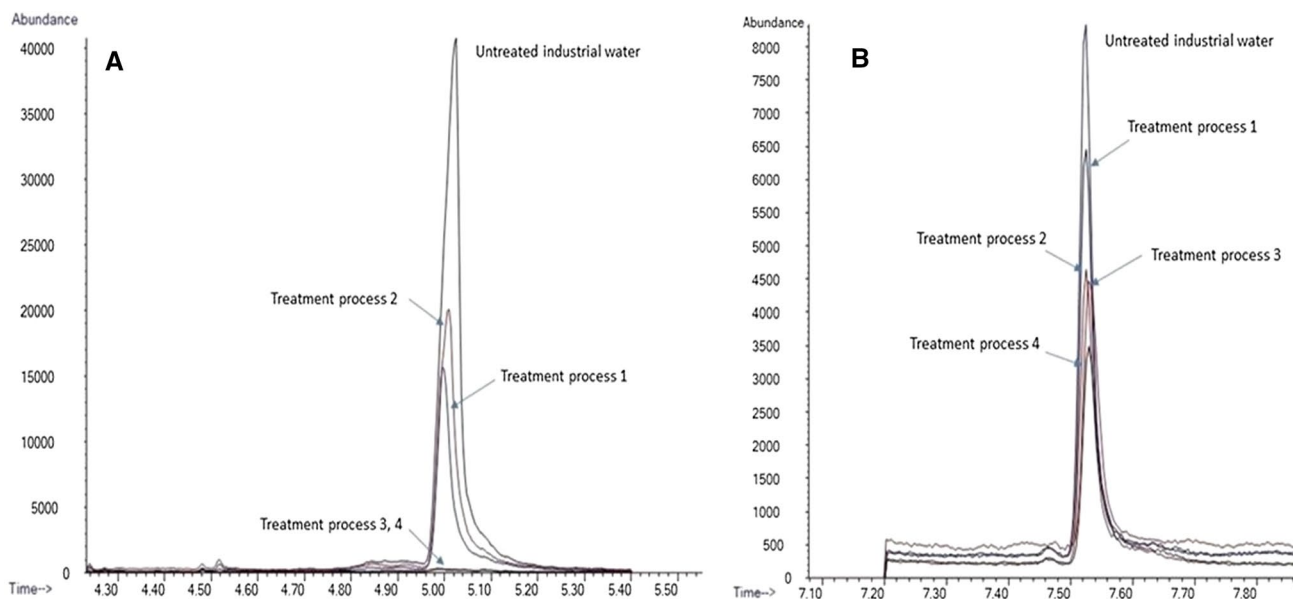
	Procedure 1	Procedure 2	Procedure 3	Procedure 4
Marker i	REF_i (TW1)/%	REF_i (TW2)/%	REF_i (TW3)/%	REF_i (TW4)/%
Adipol 2EH	24.1 weak	38.1 moderate	50.1 moderate	77.0 significant
Oleic acid	85.1 significant	93.2 significant	99.6 significant	99.5 significant
Palmitic acid	30.9 moderate	63.8 moderate	51.3 moderate	57.1 moderate
Ethylene glycol monododecyl ether	57.5 moderate	31.8 moderate	99.3 significant	99.3 significant
Diethylene glycol dibenzoate	54.3 moderate	35.8 moderate	99.4 significant	99.6 significant

addition of organic acid during the treatment procedure (treatment 1 and 2) only moderate removal was achieved. The same behavior was observed for the removal of ethylene glycol monododecyl ether by the treatment procedures (1–4). In all cases, moderate removal was observed for palmitic acid (REF of 30.9–63.8%), with the best results in procedure 2 when organic acid was used during the treatment procedure. For all of the markers, significant removal was obtained with procedure 4, except for palmitic acid. It can be observed that the worst results were obtained when organic additives were used (procedure 1 and 2). However, with inorganic additives (procedure 3 and 4) the elimination of pollutants from industrial water was more effective. In comparison with the untreated industrial water, the peak areas of the pollutants were decreased in all cases, except for stearic acid, which was not selected as a marker but its chromatographic peak area changes were also studied. The

increase of the peak area of stearic acid during the treatment procedure is explained by the degradation of oleic acid. Oleic acid is usually hydrogenated directly to stearic acid without the formation of trans fatty acid intermediates. It was shown that low pH conditions increase the conversion of oleic acid to stearic acid [24].

For illustration, the extracted ion chromatograms for ethylene glycol monododecyl ether (significant elimination) and Adipol 2EH (moderate removal) are plotted in Fig. 4 to show the removal effects during the four different treatment processes.

The results have shown that with all four types of treating procedure the amount of the organic compounds was reduced. For illustration, Fig. 5 shows the TIC chromatograms obtained for the untreated and the treated industrial water sample. The industrial water effluent showed lots of

**Fig. 4** Elimination of ethylene glycol monododecyl ether (**A**) and Adipol 2EH (**B**) during the treatment procedures

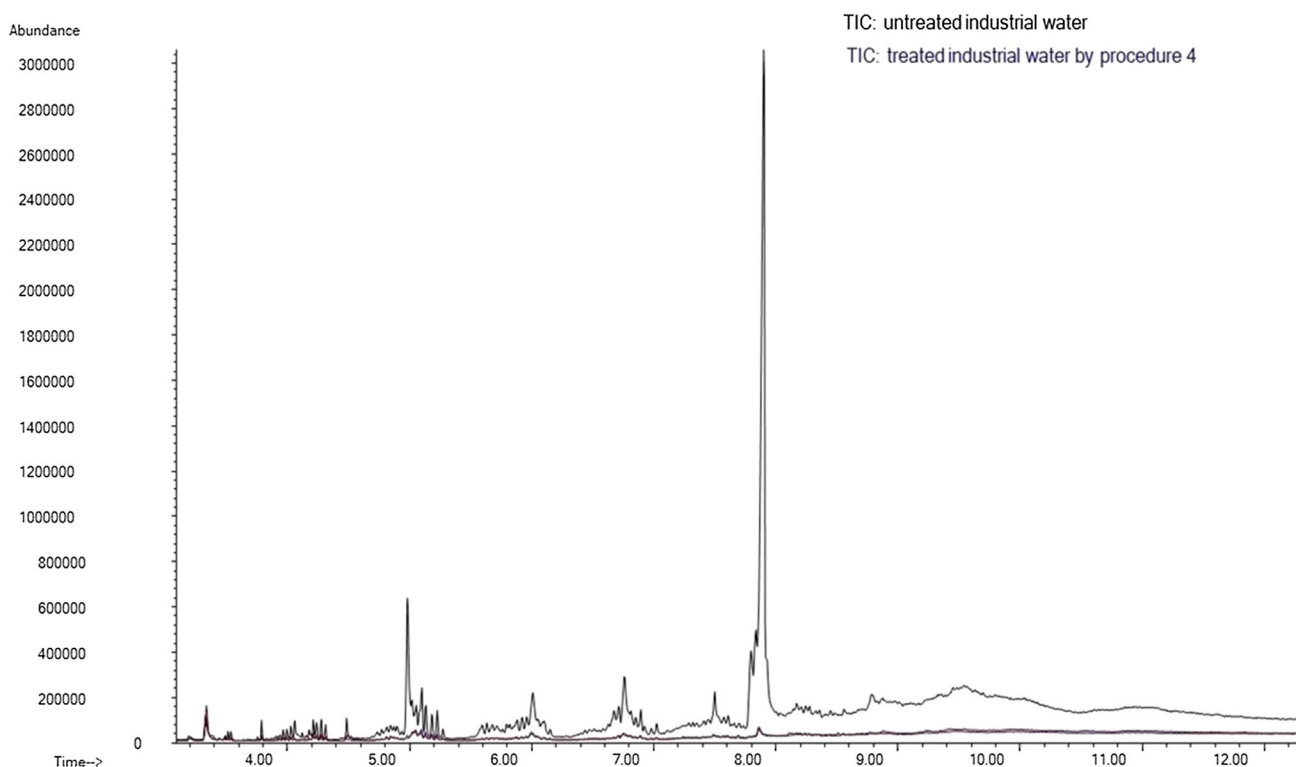


Fig. 5 Total ion chromatogram of the LLE extract of raw industrial water and industrial water treated with procedure 4

chromatographic peaks which were partially or completely removed during the treating procedure.

Conclusion

The occurrence of organic pollutants in industrial water samples was studied by LLE–GC–MS. Several extraction parameters were tested and the best parameters were selected for the isolation of the analytes from industrial water effluent. Five compounds were identified and selected as markers. For the treatment procedures, a new ecological technology based on the application of electro-thermochemical technology was used to remove organic pollutants from industrial water. For evaluation purposes, removal efficiency factors were defined and markers removal was evaluated in terms of weak, moderate and significant. It was found that the removal factors REF_i of the selected markers are in some cases higher than 90% and thus, significant removal was obtained, indicating a promising way for further technology upgrade. The procedure is fully aligned with the principle of circular and green economy, which is at the center of interest of the world's climate policies and wastewater recycling efforts. Traditional wastewater treatment technologies produce sludge, which is disposed of by burning and produces emission gases. Electro-thermochemical technology offers

a greener solution for waste valuation and disposal. The best results were obtained with inorganic additives were used during the treatment procedures. Industrial water treatment and reuse applications, besides the economic benefit, have ecological benefits due to sustainable water management: reduction of the consumption of water resources and reduction of wastewater discharges into natural water bodies.

Materials and methods

Analytical standards of the following analytes, stearic acid, oleic acid, palmitic acid, Adipol 2EH, ethylene glycol monododecyl ether, diethylene glycol dibenzoate with purity higher than 95% were obtained from (Merck KGaA, Darmstadt, Germany). First, the standard stock solution of individual analytes was prepared at a concentration of 1 mg cm^{-3} in toluene (Merck KGaA, Darmstadt, Germany), from which the composite stock standard solution at a concentration of 0.020 mg cm^{-3} in toluene was prepared. Stock solutions were stored in the freezer at $-18 \text{ }^\circ\text{C}$; diluted working solutions were prepared daily and stored in the fridge at $+4 \text{ }^\circ\text{C}$. Solvents with different polarities, toluene, (Merck KGaA, Darmstadt, Germany); hexane, dichloromethane, and acetonitrile (all from Sigma Aldrich, Steinheim, Germany) were used for the extraction. All the solvents and also

purified water (Sigma Aldrich, Steinheim, Germany) were of reagent grade purity. Sodium chloride (NaCl)—per analysis (Lachema a.s., Brno, Czech Republic) was baked at 600 °C (6 h) in the muffle furnace.

Samples

Samples of the industrial water effluent were obtained from the paint industry Slovák Košeca, a.s. The samples were directly collected from the water tanks. Effluents were of pink color and had a COD value of 60 g dm⁻³. The samples were collected into 1000 cm³ prewashed glass bottles, shipped to the lab, stored at 4 °C in the fridge. In total, 40 dm³ of samples were collected. Prior to analysis, samples were filtrated through a 0.45 µm cellulose membrane filter (GF/F, Whatman, UK).

Industrial water treatment

For electro-thermochemical treatment experiments, a portion of the samples (20 dm³ in total) were utilized. The industrial water effluent was divided into two parts and organic, resp. inorganic additives were added to the samples during the treatment procedure. Both additives were used at two different treatment times and with the same electrical parameters resulting in four treated water samples at the end of the procedure. Samples 1 and 2 were treated with an organic acid and samples 3 and 4 with an inorganic salt.

The nature of particular additives and the particular technology parameters are a subject of the intellectual property of Hofitech.

Liquid–liquid extraction

To isolate analytes of interest from both, the raw untreated industrial water effluent and the treated samples, an LLE technique was applied. A volume of 8 cm³ of filtered water samples (either untreated or treated) was poured into a 15 cm³ polypropylene centrifuge tube. The volume of 3 cm³ of extraction solvent toluene (alternatively dichloromethane, hexane, and acetonitrile for optimization studies) was added to the tube. Immediately afterward, vortex mixing (20 min, 1500 rpm) was used for intensifying the dispersion of the extraction solvent into the sample. Subsequently, the mixture was centrifuged (ROTOFIX 32; Hettich centrifuge, Tuttlingen, Germany) at 4000 rpm for 5 min. The final toluene extract was transferred to the 2 cm³ vial and analyzed by GC–MS analysis.

GC–MS analysis

GC–MS analyses were accomplished on Agilent 6890 gas chromatograph (Agilent, Little Falls, DE, USA) coupled to

mass selective detector Agilent 5975 (Agilent, Little Falls, DE, USA) equipped with programmable temperature vaporization (PTV) injector. A multi baffle deactivated PTV liner without glass wool was used, obtained from Agilent (Agilent, Little Falls, DE, USA).

Agilent 7683B autosampler was used for the injection of 2 mm³ of LLE extracts in solvent vent injection mode with a purge flow 50 cm³ min⁻¹ at 1.75 min. The PTV temperature program was the following: 40 °C (hold 0.20 min), 400 °C min⁻¹ to 300 °C (hold 2.00 min), and 400 °C min⁻¹ to 350 °C (hold 5.00 min).

A capillary column (15 m × 0.15 mm I.D. × 0.15 µm film thickness) with 5% diphenyl 95% dimethylsiloxane stationary phase (CP-Sil 8 CB; Agilent Technologies, Middelburg, Netherlands) connected to a non-polar deactivated precolumn (1 m × 0.32 mm I.D.) was used. The oven temperature program used for the analyses was set as follows: 60 °C held for 1.75 min, increased at 60 °C min⁻¹ to 150 °C, then increased at 23.8 °C min⁻¹ to 300 °C and held for 1.90 min. Helium was used as the carrier gas at a constant flow of 1.2 cm³ min⁻¹.

The mass spectrometer was operated in electron ionization mode (70 eV). The ion source temperature was maintained at 250 °C. For a full scan, the mass range of $m/z = 40\text{--}550$ was selected. In selected ion monitoring (SIM) mode, ions were sorted into groups; the dwell time used was 10 ms.

Identification of pollution markers

Identification of individual compounds was based on a comparison of the acquired mass spectra with those from standards and from the NIST library applying library search options (National Institute of Standards and Technology, Gaithersburg, MD, USA).

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References

1. Kong Z, Li L, Xue Y, Yang M, Li YY (2019) J Clean Prod 231:913
2. Subki NS, Akhir NM, Halim NSA, Yusoff NRN (2020) IOP Conf Ser Earth Environ Sci 549:012066
3. Sun Y, Zhou S, Sun W, Zhu S, Zheng H (2020) Sep Purif Technol 241:116737
4. Li J, Pham AN, Dai R, Wan Z, Waite TD (2020) J Hazard Mater 392:122261
5. Sheth Y, Dharaskar S, Khalid M, Sonawane S (2021) Sustain Energy Tech 43:100951

6. Gondal MA, Hussain T (2007) *Talanta* 71:73
7. Mohsen AELS, Hasanin EA, Kamel MM (2010) *Am Eurasian J Agric Environ Sci* 8:597
8. Vishali S, Roshini SK, Samyuktha MR, Ashish K (2018) *Environ Monit Assess* 190:587
9. Monga D, Basu S (2019) *Adv Powder Technol* 30:1089
10. Wang Y, Ding K, Xu R, Yu D, Wang W, Gao P, Li B (2020) *J Clean Prod* 247:119108
11. Sharma S, Simsek H (2019) *Chemosphere* 221:630
12. Ahmad T, Belwal T, Li L, Ramola S, Aadil RM, Xu Y, Zisheng L (2020) *Trends Food Sci Tech* 99:21
13. An C, Huang G, Yao Y, Zhao S (2017) *Sci Total Environ* 579:537
14. Ahmad M, Bajahlan AS, Hammad WS (2008) *Environ Monit Assess* 147:297
15. Makoś P, Przyjazny A, Boczkaj G (2018) *J Chromatogr A* 1570:28
16. Pothitou P, Voutsas D (2008) *Chemosphere* 73:1716
17. Nurerk P, Llompart M, Donkhampa P, Bunkoed O, Dagnac T (2020) *J Chromatogr A* 1610:460564
18. Randall PM (1992) *J Hazard Mater* 29:2755
19. Noruzman AH, Apandi NM (2020) *J Adv Res Bus Managem Stud* 20:28
20. Krithika D, Philip L (2016) *Int Biodeter Biodegr* 107:31
21. Lin KF (2016) *Alkyd resins*. Kirk-othmer encyclopedia of chemical technology. John Wiley and Sons, New Jersey
22. Dalgaard M, Hass U, Vinggaard AM, Jarfelt K, Lam HR, Sørensen IK, Sommer HM, Ladefoged O (2013) *Reprod Toxicol* 17:163
23. Ghisari M, Bonefeld-Jorgensen EC (2009) *Toxicol Lett* 189:67
24. AbuGhazaleh AA, Riley MB, Thies EE (2005) *J Dairy Sc* 88:4334

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