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New Procedures for Control of Industrial Effluents Treatment Processes

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Supporting Information

ABSTRACT: This work presents the procedures for monitoring volatile organic compounds during treatment of industrial effluents. The investigation was carried out for a specific effluent—caustic effluent from bitumen production. The developed procedures enable more detailed control of the effectiveness of wastewater treatment than standard procedures. Caustic effluents from bitumen production have a complex physicochemical form and consist of an emulsion of an organic phase in a strongly alkaline aqueous phase. The occurrence of an emulsified organic phase in the aqueous phase of the effluents results in their high toxicity toward the activated sludge of a refinery wastewater treatment plant as well as strong malodorousness. Interpretation of analytical results reveals that the effluents contain over 400 organic compounds among volatile organic compounds (VOCs) alone. Using the developed procedures, 114 of the VOCs were identified in raw postoxidative effluents. The procedures described in this work allow detailed identification of VOCs as well as the determination of distribution of their concentrations for individual classes of chemical compounds. Monitoring changes in content of individual classes of VOCs, including highly malodorous volatile sulfur compounds, as well as changes in total VOC content, provides more information on the processes taking place during wastewater treatment.

1. INTRODUCTION

Many aspects of environmental protection involve minimization of the effect of industry on the environment. The predominating nature of the effect depends on the type of industry, but in the majority of cases the effects are mostly similar. The most important effects include emission of air pollutants, emission of pollutants in wastewater and infiltration through the soil, and noise pollution.

In each case, identification of major threats and evaluation of the magnitude of their negative effect are required. Identification of gaseous and liquid pollutants is necessary in order to select appropriate measures of environmental protection.[1−4] Monitoring of transformation of pollutants undergoing treatment is also important.[5−7] Chromatographic techniques have been widely used for screening of pollutants.[8−24] Gas chromatography plays a particularly important role in control of effluent treatment processes in case of occurrence of volatile organic compounds (VOCs).[17,25−29] Electronic noses have also been used in monitoring of the composition of industrial effluents.[30] Monitoring of nonvolatile compounds in effluents is accomplished by liquid chromatography or flow injection analysis. Mass spectrometry is most frequently employed for identification purposes.[31−33] The determination of concentrations and concentration changes of selected groups of contaminants during wastewater treatment can also make use of other selective detection techniques.[34]

This work describes detailed identification of volatile organic compounds and determination of changes in their content during treatment of effluents from the production of bitumen using dynamic headspace and gas chromatography−mass spectrometry (DHS-GC-MS). Identification was appended with the results of investigations employing GC detectors selective toward sulfur- and nitrogen-containing compounds. Procedures for monitoring changes in content of VOCs in the effluents resulting from wastewater treatment and based on the measurement of headspace concentrations of VOCs have also been developed.

The investigation was carried out for a specific kind of effluents—the alkaline effluent from the production of bitumen. Characteristics of operations and processes resulting in formation of this type of effluents were described in a previous work.[17] As a result of high loads of pollutants, attempts at preliminary treatment of the effluent prior to feeding it to the wastewater treatment plant are being undertaken. One of the operations under consideration is effluent demulsification in order to separate the organic phase occurring in the effluents. This would result in a substantial decrease in the load of pollutants, thus lowering the cost of treatment of this kind of effluents. The analysis of changes in composition of the headspace above the effluents resulting from the removal of the organic phase is presented as an example of procedures described in this work.

2. MATERIALS AND METHODS

2.1. Materials. The following materials were used in this study: (1) carbon disulfide (GC grade, Fluka Analytical, Neu-Ulm, Germany); (2) standards of volatile organic compounds

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(Sigma Aldrich, St. Louis, USA); (3) compressed gases helium, nitrogen, air of 5.0 N purity grade (Linde Gaz, Cracow, Poland), and hydrogen of 5.5 N purity grade from a hydrogen generator (Packard, Downers Grove, USA); (4) Tedlar bags (SKC Inc., Eighty Four, USA); (5) 22 mL headspace vials with caps equipped with a dpoly(tetrafluoroethylene) (PTFE)-lined silicone septum (BGB Analytic, Boeckten, Switzerland).

2.2. Apparatus. The equipment used is detailed as follows: (1) a model HP 5890 gas chromatograph with a model HP 5972A mass spectrometer (Hewlett-Packard, Wilmington, DE, USA), Chemstation software (Agilent, Santa Clara, CA, USA), and NIST 05 and Wiley 8.0 mass spectra libraries; (2) an Autosystem gas chromatograph with a flame ionization detector (FID) and nitrogen−phosphorus (NPD) detector (Perkin-Elmer, Waltham, Massachusetts, USA), A/C Nelson 900 interface (Perkin-Elmer, Waltham, Massachusetts, USA), and Totalchrom software; (3) a model GC 8500 gas chromatograph with FID (Perkin-Elmer, Waltham, Massachusetts, USA), A/C Nelson 900 interface (Perkin-Elmer, Waltham, Massachusetts, USA), and Totalchrom software; (4) a model G1901-60502 purge and trap concentrator (Hewlett-Packard, Wilmington, DE, USA); (5) GC capillary columns [K1, 60.0 m × 0.25 mm × 0.25 μm DB5 ms (Agilent, Santa Clara, CA, USA); K2, 60.0 m × 0.32 mm × 1.0 μm HP1 (Hewlett- Packard, Wilmington, DE, USA); K3, 30.0 m × 0.32 mm × 1.00 μm PE-5 (Perkin-Elmer, Waltham, Massachusetts, USA); K4, empty fused silica capillary 30.0 m × 0.32 mm (BGB, Boeckten, Switzerland)].

2.3. Procedure. *2.3.1. Identification of Volatile Components of Postoxidative Effluents by Dynamic Headspace and Gas Chromatography−Mass Spectrometry.* Samples (5 mL) of the effluents were placed in 10 mL vials. Next, the vials were closed with screw caps equipped with a PTFE-lined silicone septum. Two fused silica capillaries were introduced through the septum—one of them fed helium purging the effluent sample while the other one transported the gas with the analytes to a sorbent trap. The purging process was carried out at 25 °C for 10 min. The sorbent trap was maintained at 30 °C. During thermal desorption the trap was initially heated to 260 °C, and the analyte desorption from the trap was performed at 270 °C for 4 min. The desorbed analytes were passed through a fused silica transfer line heated to 200 °C directly to the gas chromatograph.

Separation Conditions. The following separation conditions were used: (1) column K1; (2) carrier gas of helium at 1.1 $\mathrm{cm^3/min}$; (3) injection port temperature of 300 °C (connection of purge and trap accessory to GC); (4) temperature program of 40 °C (5 min.), ramped at 5 °C/min to 250 °C (15 min.).

Mass Spectrometric Detection. The following conditions for mass spectrometric detection were used: (1) ion source temperature (EI, 70 eV) of 200 °C and GC-MS transfer line temperature of 310 °C; (2) SCAN mode from mass-to-charge ratio of 34−300 m/z.

Three independent determinations were carried out for each of the investigated sewage samples. Analyte identification was based on comparison of mass spectra of the analytes with those in the NIST and Wiley mass spectra libraries. Peak areas of identified analytes were calculated for selected ions characteristic of a particular analyte.

2.3.2. Identification of Volatile Sulfur Compounds Using Static Headspace and Gas Chromatography with Pulsed Flame Photometric Detector. Effluent samples (10 mL) were thermostatted in capped 22 mL headspace vials at 80 °C for 30 min. Next, 0.5 mL headspace samples were collected using a gastight syringe heated to 100 °C. The samples were immediately introduced into the injection port of gas chromatograph.

Separation Conditions. The following separation conditions were used: (1) column K2; (2) carrier gas of helium at 1.2 $\mathrm{cm^3/min}$; (3) injection port temperature of 300 °C; (4) temperature program of 40 °C (7 min.), ramped at 5 °C/min to 260 °C and ramped at 30 °C/min to 300 °C (5 min).

PFPD Operating Parameters. The PFPD operating parameters were as follows: (1) detector temperature of 300 °C and gas pressures for hydrogen of 21.0 psig, for air of 12.6 psig, and for makeup gas (air) of 14.8 psig; (2) signal acquisition parameters for photomultiplier tube voltage of 600 V, for a pulse rate of 3.57 Hz, and for the sulfur chemiluminescence gate width of 6−24 ms.

A detailed description of the procedure and method validation is provided in ref 17.

2.3.3. Identification of Volatile Nitrogen Compounds by Static Headspace and Gas Chromatography with Nitrogen−Phosphorus Detector . Effluent samples (10 mL) were thermostatted in capped 22 mL headspace vials at 80 °C for 30 min. Next, 0.5 mL headspace samples were collected using a gastight syringe heated to 100 °C. The samples were immediately introduced into the injection port of the gas chromatograph.

Separation Conditions. The following separation conditions were used: (1) column K3; (2) carrier gas of helium at 2.0 $\mathrm{cm^3/min}$; (3) injection port temperature of 300 °C; (4) temperature program of 45 °C (2 min), ramped at 10 °C/min to 285 °C (15 min).

Operating Parameters of NPD. The operating parameters of the nitrogen-phosphorus detector (NPD) were as follows: detector temperature of 300 °C and gas flow rates for hydrogen of 3.5 $\mathrm{cm^3/min}$ and for air of 85 $\mathrm{cm^3/min}$.

Three independent determinations were performed for each analysis. Analyte identification was based on comparison of retention times with those for a standard mixture.

Concentrations of volatile nitrogen compounds in the headspace were calculated using response factors for the NPD detector.

The limit of detection (LOD) was calculated from eq 1:

$$\mathrm{LOD} = 3\frac{S}{N} \tag{1}$$

where S is the analyte signal (pA) and N is noise near the analyte retention time (pA). The limit of quantitation (LOQ) was calculated from eq 2:

$$\mathrm{LOQ} = 2\mathrm{LOD} \tag{2}$$

The response factor was calculated from eq 3:

$$R_{\mathrm{f},i} = \frac{\overline{A}_i}{m_i} \tag{3}$$

where $R_{\mathrm{f},i}$ is the response factor of analyte i (μV·s/ng), $\overline{A}_i$ is the average value (n = 3) of the peak area of analyte i (μV·s), and m_i is the mass (ng) of analyte i introduced into the GC.

The response factors per nanogram of analyte as well as their limits of detection and quantitation determined for four volatile nitrogen compounds are compiled in Table 1.

In procedures based on headspace analysis, there is a strong effect of the matrix composition on the solution−headspace equilibrium. In the case of industrial effluents of a variable

Table 1. Compilation of Experimental Response Factors and Limits of Detection and Quantification for Four Standard VOCs

compound	$R_{f,i}$[a] (μV·s/ng)	RSD (%)	LOD[b] (pg (ppm))	LOQ[c] (pg (ppm))
acetonitrile	758918	3.4	48 (0.06)	96 (0.11)
pyridine	987811	3.1	32 (0.02)	64 (0.03)
2-methylpyridine	688812	3.3	51 (0.03)	102 (0.05)
2,4-dimethylpyridine	521700	3.1	64 (0.03)	128 (0.06)

[a] $R_{f,i}$ = response factor. [b] LOD = detection limit. [c] LOQ = quantification limit.

composition and pH (10.0−11.5), the ratio of partition coefficients of individual compounds with respect to a specific internal standard will not be constant. For this reason, the internal standard method was not used in this work.

The proposed procedure is based on comparison of concentrations determined directly in the headspace for raw effluent and that after treatment.

2.3.4. Determination of Total Content of Volatile Organic Compounds by Static Headspace and Gas Chromatography with Flame Ionization Detector. Effluent samples (10 mL) were thermostatted in capped 22 mL headspace vials at 50 °C for 30 min. Next, 0.5 mL headspace samples were collected using a gastight syringe heated to 80 °C. The samples were immediately introduced into the injection port of the gas chromatograph.

Separating Conditions. The following separation conditions were used: (1) column K4; (2) injection port temperature of 300 °C and split injection mode (5:1); (3) oven temperature of 275 °C; (4) carrier gas of helium at 5.0 cm^3/min.

Operating Parameters of FID. The FID operating parameters were as follows: detector temperature of 300 °C, gas flow rates for hydrogen of −40 cm^3/min and for air of −450 cm^3/min.

The concentrations of volatile organic compounds in the headspace were determined using the external standard method (five-point calibration curve). Methane in air was used as the standard gas. In order to test the accuracy of determinations making use of a universal calibration with methane to determine total VOC content, the results were compared with the ones for a standard mixture containing eight chemical compounds.

Preparation of Standard Mixtures. Standard gaseous mixtures were prepared by injecting liquid standard compounds into a Tedlar bag using a microsyringe. Eight compounds with varying polarities, boiling points, and structures were selected: 2-propanethiol, hexane, 2-propanol, cyclohexane, 2-butanone, toluene, 2-methylpyridine, and acetonitrile. Tedlar bags were filled with synthetic air introduced by means of a gastight syringe from a compressed air tank through a septum installed on a gas line. The composition of the primary standard mixture was calculated from the amounts of standards introduced, assuming their complete evaporation. Other standard mixtures were prepared by successive injections of known volumes of a more concentrated standard mixture into another Tedlar bag filled with synthetic air. In this way, gas standards with total concentrations of 10, 100, and 1000 ppm were prepared. Prior to usage, Tedlar bags were cleaned five times by repeating a cleaning cycle consisting of filling the bag with high purity nitrogen, leaving it for 30 min, and emptying it using a vacuum pump. Prior to preparation of standard gaseous mixtures, the Tedlar bag background was checked by carrying out three analyses of air using GC-FID.

Analytical characteristics of the procedure for the determination of total VOCs are discussed in the following sections.

Linearity. Linearity of the procedure was examined in the total VOC content range described above using the prepared standard mixture and relative to the calibration mixture (methane in air), against which quantitative analysis was carried out. Linearity of the detector response in the investigated range was estimated from the regression coefficient (r), which should be equal to or close to one. For the investigated procedure, this assumption was met in the range 1−10^4 ppm.

Limit of detection and quantitation of the GC-FID procedure for determination of the total VOC content was calculated as follows.

The detection limit (LOD) was calculated from eq 4:

$$\mathrm{LOD} = \frac{3.3 s_a}{b} \tag{4}$$

where LOD is the limit of detection, s_a is the standard deviation of the intercept of the calibration curve, and b is the slope of the calibration curve.

The limit of quantitation (LOQ) was calculated from eq 2.

Table 2 lists numerical values of the investigated validation parameters.

A comparison of the characteristics of FID responses for the standard VOC mixture and for methane reveals that the total VOC content can be calculated from the calibration curve obtained for methane in air.

2.3.5. Effluent Demulsification. Effluent of 150 mL volume was mixed in a separatory funnel with 15 mL of a 0.2% (w/w) solution of industrial demulsifier for refinery effluents. After 5 min of manual shaking, the emulsion was left to stand to accomplish phase separation. The lower fraction—the effluent devoid of organic phase—was transferred to tightly closed vials. Following demulsification operation, the postoxidative effluent had the appearance of a clear aqueous phase. Raw and demulsified effluents were stored in the vials at 4 °C until analysis. The determinations were carried out in time not exceeding 24 h after demulsification.

2.3.6. Determination of Percent Reduction in VOC Content by Effluent Demulsification Using DHS-GC-MS. Individual chromatographic peaks were identified by comparison of their mass spectra with those in the NIST and Wiley libraries. Two characteristic mass-to-charge ratio values were selected for each compound. This formed the basis for VOC

Table 2. Comparison of Regression Parameters of Calibration Curves

mixture	slope	intercept	R^2[a]	LOD (mg/m^3)	LOQ (mg/m^3)	LOQ (ppm)
methane in air	154.34 ± 0.78	0.134 ± 0.024	0.999	0.6	1.2	1.8
mixture of VOCs in air	150.12 ± 0.79	0.70 ± 0.23	0.999	1.1	2.2	0.7

[a] R_2 = determination coefficient.

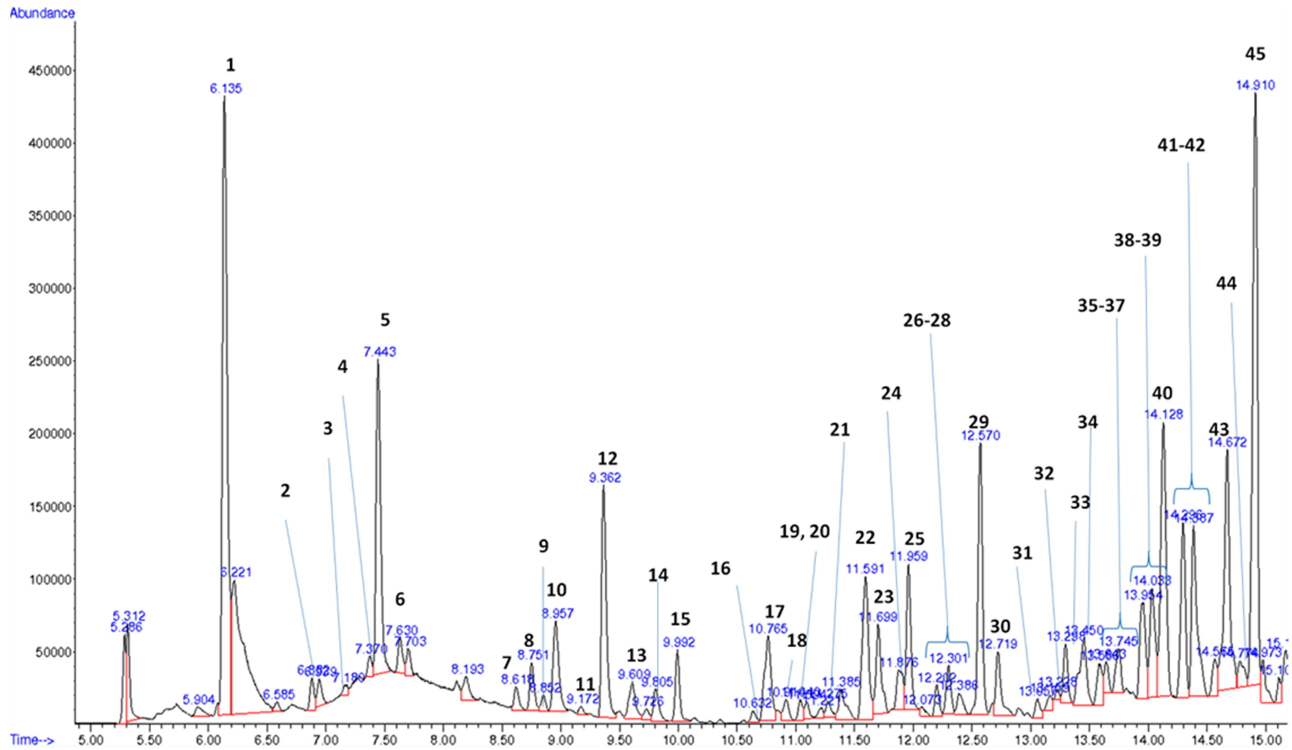

Figure 1. DHS-GC-MS chromatogram of raw postoxidative effluent, enlarged between 5 and 15 min. Identified compounds: (1) propanone; (2) 2-methylpropanal; (3) 2,5-dihydrofuran; (4) butanal; (5) 2-butanone; (6) 2-butanol; (7) 3-methylbutanal; (8) 3-methylbutanone; (9) 2-methylbutanal; (10) benzene; (11) 2-methylhexane; (12) 2-pentanone; (13) 2-methylpentenal; (14) 2-ethoxy-1-propanol; (15) heptane; (16) methylcyclohexane; (17) methyl isobutyl ketone; (18) dimethyl disulfide; (19) 2-methyl-3-pentanone; (20) 3-ethoxy-2-methylpropene; (21) 2-isopropyl-2-methyloxirane; (22) toluene; (23) 2-methylheptane; (24) 3-hexanone; (25) 2-hexanone; (26) 2,5-dimethylhexane; (27) *cis*-1-butyl-2-methyl-cyclopropane; (28) 3-methyl-2-heptanol; (29) octane; (30) 2-methylhexanal; (31) 3,5-dimethylcyclohexane; (32) ethyl methyl sulfide; (33) 2,6-dimethylheptane; (34) 5-methyl-2-hexanone; (35) 1,1,3-trimethylcyclohexane; (36) 2-heptanone; (37) 2-nonene; (38) ethylbenzene; (39) 1-octene; (40) *p*-xylene; (41) 3-methyloctane; (42) 3-heptanone; (43) *o*-xylene; (44) 2-ethyl-2-pentenal; (45) nonane.

identification. Integration of chromatographic peaks was based on the detector signal counted only for the selected ions for each compound. The results were compared for the investigated effluent before and after removal of the organic phase.

The headspace concentrations determined for volatile sulfur compounds (VSCs), volatile nitrogen compounds (VNCs), and total VOCs are reported in units of mass per headspace volume and also converted to mole fractions in the headspace using eq 5

$$C/\text{ppm} = \frac{24.45[C/(\text{mg/m}^3)]}{M} \qquad (5)$$

where M is the molar mass of a compound (g/mol). Conversion to parts per billion takes place after substitution in eq 5 concentration expressed in (μg/m^3).

3. RESULTS AND DISCUSSION

Caustic postoxidative effluents are a complex mixture consisting of a strongly basic aqueous phase containing a high concentration of sulfides (from absorption of hydrogen sulfide), volatile organic compounds, and a condensate of oil mist and bitumen microdrops carried from the oxidation reactor by a stream of vapors. Microscopic examination of the effluent morphology revealed that the effluent is a stable emulsion of the organic phase in the aqueous phase. Formation of the emulsion can likely be attributed to the presence in the effluent of surfactants formed during the oxidation process, i.e., long-chain aldehydes or carboxylic acids. Postoxidative effluents (alkaline absorbate), prior to being fed to a wastewater treatment plant, are recycled in a scrubber in which waste gases are washed from the bitumen oxidation installation. Pumping the effluent intensifies the process of emulsification of the organic phase in the aqueous phase. Depending on the intensity of the oxidation process, fresh batches of lye are added to the cycled absorbate, and excess effluent is removed from the installation. After preliminary isolation of the oil condensate in a plate separator, the effluents are fed to a wastewater treatment plant. The effluents undergo several stages of treatment, including physical separation of the oil phase, flocculation, biological treatment, and clarification. As a result of strong emulsification of the effluent, classical methods of wastewater treatment are not sufficiently effective for postoxidative effluents. Consequntly, biological treatment is performed on the effluent with excessively high load of organic pollutants. Specifically, high biotoxicity and malodorousness of the effluents call for their preliminary treatment prior to introduction into a wastewater treatment plant. This, in turn, requires the development of an effective technology of effluent pretreatment, ensuring a significant reduction in their malodorousness and biotoxicity.

This work describes analytical procedures allowing more effective control of the pretreatment effectiveness than the standard procedures permit. In many cases, process control of the effectiveness of effluent pretreatment is accomplished by determining standard water quality parameters, such as

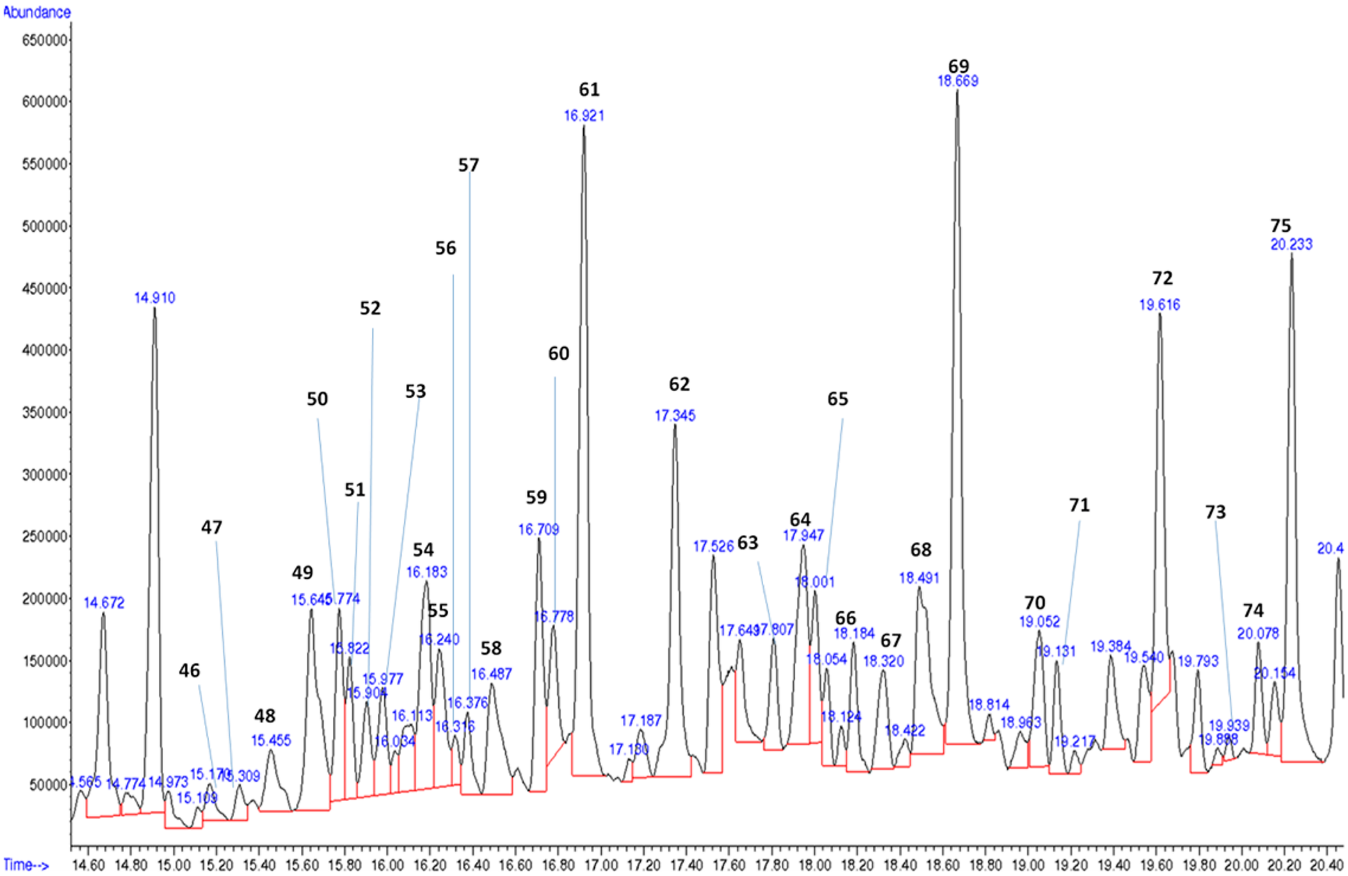

Figure 2. DHS-GC-MS chromatogram of raw postoxidative effluent, enlarged between 15 and 20 min. Identified compounds: (46) 1,2-dimethyl-3-(1-methylethyl)cyclopropane; (47) 4-methoxy-4-methyl-1,3-pentadiene; (48) 2-methyl-2-oxazoline; (49) cyclohexanone; (50) 6-methyl-2-heptanone; (51) benzaldehyde; (52) pentylcyclopentane; (53) propylbenzene; (54) 4-methylnonane; (55) 1,1,2,3-tetramethylcyclohexane; (56) 2,6-dimethyl-2,6-octadiene; (57) 5-methyl-3-heptanone; (58) 1-ethyl-4-methylbenzene; (59) cyclodecane; (60) 1,2,4-trimethylbenzene; (61) decane; (62) 1,2,4-trimethylbenzene; (63) 2-methylcycloheptanone; (64) acetophenone; (65) 2-methylbenzaldehyde; (66) 3-methylbenzaldehyde; (67) 2-nonanone; (68) 1-ethyl-2,4-dimethylbenzene; (69) undecane; (70) 1,2,4,5-tetramethylbenzene; (71) 1,2,4,6-tetramethylbenzene; (72) 4-methylundecane; (73) 1-ethyl-3,5-dimethylbenzene; (74) 1-(4-methylphenyl)ethanone; (75) 2-butyl-1-octanol.

biological oxygen demand (BOD) and chemical oxygen demand (COD). However, BOD and COD are not good measures of the effectiveness of effluent treatment aimed at reduction of malodorousness, i.e., reduction of specific groups of VOCs as well as their total content.

No works characterizing the composition of caustic effluents from the bitumen production have been published thus far. Examination of the effluent composition provides additional information on the components formed during bitumen oxidation by thermal cracking and oxidation of the resulting chemical compounds. The analysis of raw composition of the effluents allows estimating environmental hazards associated with possible emission of volatile components from the effluents during treatment processes carried out in open basins. This pertains especially to biological stages of wastewater treatment (activated sludge process).

The effluent from the bitumen production studied in this project were collected from industrial scale installation for the bitumen oxidation behind the pump transporting the effluent to a corrugated plate separator, used for the removal of organic phase condensate from the effluent stream. As was mentioned earlier, this kind of separation of organic phase is ineffective for postoxidative effluent, which contains the organic phase not only in the form of condensate, but also in the form of emulsion in the aqueous phase of the effluent. Under industrial conditions, demulsification as a step of pretreatment of postoxidative effluent should precede separation by a corrugated plate separator. This way, both the condensate as well as the organic phase separated from the effluent through demulsification would be removed. The results of large laboratory-scale investigations on demulsification of postoxidative effluents will be the subject of future papers. Demulsified effluent devoid of organic phase can be pumped to a wastewater treatment plant and subjected to biological treatment. If demulsified effluent has to be treated further to remove the pollution load, it can be subjected to other pretreatment stages, e.g., through oxidation.

3.1. Identification of VOCs in Postoxidative Effluents Using Dynamic Headspace Followed by Gas Chromatography–Mass Spectrometry. Identification of VOCs in postoxidative effluents was carried out by using dynamic headspace coupled with gas chromatography–mass spectrometry (DHS-GC-MS). The effectiveness of analyte enrichment by purge and trap depends mostly on analyte volatility. Inspection of *n*-alkanes identified by GC-MS revealed that the heaviest *n*-alkane released from the effluents by purge and trap is *n*-tetradecane (n-C_{14}; boiling point, 254 °C).

In the case of using dynamic headspace technique, a negative effect of water vapor on the sorption capacity of the trap is well documented, even when using hydrophobic sorbents, such as

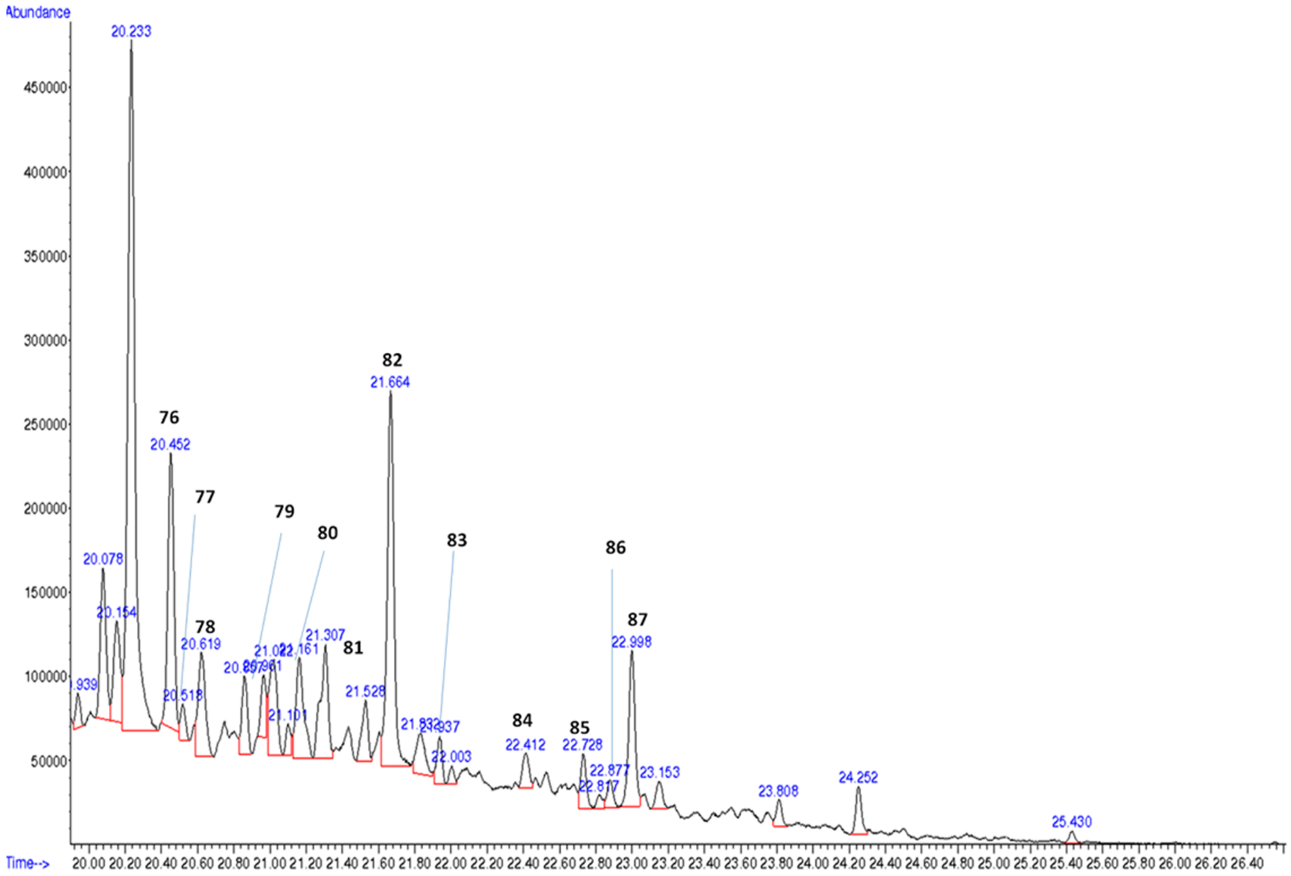

Figure 3. DHS-GC-MS chromatogram of raw postoxidative effluent, enlarged from 20 min up. Identified compounds: (76) dodecane; (77) 2,6-dimethylundecane; (78) 1,3-dimethyl-5-(1-methylethyl)benzene; (79) 1-ethyl-2,4,5-trimethylbenzene; (80) 2-butyl-1,1,3-trimethylcyclohexane; (81) hexylbenzene; (82) tridecane; (83) cyclotridecane; (84) 2,4,5-trimethylbenzaldehyde; (85) 2,4,6-trimethylbenzaldehyde; (86) 2,3,5,6-tetramethyldecane; (87) tetradecane.

Tenax TA. The use of elevated temperatures for purging the analytes from the aqueous phase is disadvantageous. It would result in a shorter time of purging but at the expense of problems with excessive amounts of water vapor introduced with the purge gas. For this reason, in order to utilize the developed procedure in routine analyses, it was decided to purge the analytes at ambient temperature, i.e., 25 °C. The sorption trap temperature during the enrichment step was set at 30 °C. This temperature ensures appropriate capacity of the sorption trap while at the same time enables rapid cooling following the thermal desorption step solely by using the built-in fan in the DHS accessory. The use of a gaseous cooling agent (vapor of liquid nitrogen, CO_2) to cool the trap to lower temperatures during routine analyses is tedious and impractical.

The use of DHS-GC-MS resulted in identification of 87 VOCs. Examples of DHS-GC-MS chromatograms of post-oxidative effluents are shown in Figures 1−3 and S1 (Supporting Information).

The results of investigation of the headspace of postoxidative effluents demonstrated the presence of a large number of volatile organic compounds. Eighty-seven VOCs were identified in raw postoxidative effluents using DHS-GC-MS. No carboxylic acids were found in the headspace above the effluents due to strongly alkaline pH of the effluents. Under these conditions, physicochemical equilibrium solution−headspace for acidic compounds is strongly shifted toward solution and ionized form. Consequently, acidic compounds are not released to the headspace, which is advantageous, since it prevents malodorous acidic sulfur compounds or carboxylic acids from being released to the environment.

Inspection of DHS-GC-MS chromatograms in Figures 1−3 reveals the presence over 300 chromatographic peaks of analytes released from raw postoxidative effluents. Identification of a larger number of compounds would require the use of a high performance capillary column with a length exceeding 100 m, preliminary fractionation of sample components prior to chromatographic separation, or the use of multidimensional separation,[24,35] e.g., coupling liquid and gas chromatography or using two-dimensional gas chromatography (GC×GC). Analyte identification based on DHS-GC-MS is supplemented by the results of investigations using highly selective nitrogen and sulfur detectors (Tables 4 and 5).

Due to the presence in the effluents of emulsified organic phase amounting to several percent of the effluent mass, the effluents are highly toxic to the activated sludge. The effluents are also characterized by high contaminant load (the average COD on the order of 12,000 mg of O_2/dm^3) and high malodorousness. The analysis of changes in content of individual volatile organic compounds in the effluents resulting from the removal of emulsified organic phase reveals that a significant reduction in the load of pollutants is possible. The use of demulsification during preliminary effluent treatment is advantageous due to low process and investment costs of implementation of such a technology and high effectiveness of reduction of pollutant content. The percent reduction in pollutant load resulting from the removal of emulsified organic

Table 3. Comparison of Removal Efficiency of Individual Classes of VOCs Resulting from Removal of Emulsified Organic Phase

compound	raw effluent $\bar{A}_1{}^a$ (n = 3),	raw effluent s^b (pA*s)	demulsified effluent $\bar{A}_1{}^a$ (n = 3)	demulsified effluent s^b (pA*s)	reduction (%)
Aldehydes					
2-methylpropanal	7674	317	6224	227	18.9
butanal	79053	3062	56928	2262	28.0
2-methylbutanal	8729	395	6985	322	20.0
3-methylbutanal	8607	334	6985	266	18.8
2-methylpentanal	39695	1558	31393	1091	20.9
hexanal	11535	477	10399	478	9.8
2-methyl-2-pentanal	23533	1073	12619	610	46.4
2-ethyl-2-pentenal	15347	619	6178	235	59.7
benzaldehyde	12713	498	4159	189	67.3
2-methylbenzaldehyde	19962	839	7375	301	63.1
4-methylbenzaldehyde	5024	185	3275	109	34.8
2,4,5-trimethylbenzaldehyde	5911	217	1587	62	73.2
2,4,6-trimethylbenzaldehyde	3042	124	1936	74	36.4
Alkanes and Alkenes					
2-methylhexane	5127	202	not found		≫99,9
heptane	8076	333	not found		≫99,9
2-methylheptane	3674	151	not found		≫99,9
2,5-dimethylhexane	4973	186	not found		≫99,9
octane	11572	426	not found		≫99,9
2,6-dimethylheptane	21247	875	not found		≫99,9
3-ethylheptane	2273	92	not found		≫99,9
3-methyloctane	20469	782	not found		≫99,9
nonane	25150	1044	not found		≫99,9
4-methylnonane	4109	176	not found		≫99,9
decane	34195	1340	501	25	98.5
undecane	29809	1112	1099	51	96.3
4-methylundecane	11489	474	not found	-	≫99,9
dodecane	19743	909	not found		≫99,9
2,6-dimethylundecane	2179	74	not found		≫99,9
tridecane	27691	930	1566	68	94.3
2,3,5-trimethyldecane	1803	80	776	33	57.0
tetradecane	2016	79	965	42	52.1
1-octene	9143	311	3129	125	65.8
4-methoxy-4-methyl-1,2-pentadiene	15347	674	6198	244	59.6
2,6-dimethyl-2,6-octadiene	8741	431	not found		≫99,9
Alcohols					
2-butanol	78349	3456	57019	2368	27.2
2-ethoxy-1-propanol	1793	67	1470	49	18.0
2-hexanol	590	22	480	21	18.6
2-butyl-1-octanol	16693	675	1536	74	90.8
Aromatic Compounds					
benzene	56787	2772	22113	1032	61.1
toluene	71637	2389	15980	630	77.7
ethylbenzene	85887	3395	6181	288	92.8
p-xylene	85887	4696	6180	264	92.8
o-xylene	22134	873	1979	94	91.1
propylbenzene	13082	533	461	24	96.5
1-methyl-3-propylbenzene	18798	765	686	37	96.4
1,2,4-trimethylbenzene	34957	1425	1719	77	95.1
1,2,5-trimethylbenzene	32927	1150	2526	108	92.3
1-ethyl-2,4-dimethylbenzene	13478	504	not found		≫99,9
1,2,4,5,-tetramethylbenzene	21102	899	1774	88	91.6
1,2,4,6-tetramethylbenzene	16472	611	not found		≫99,9
1-ethyl-3,5-dimethylbenzene	65434	2464	10901	415	83.3
1,3-dimethyl-5-(1-methylethyl)benzene	43800	1695	6205	313	85.8
1-ethyl-2,4,5-trimethylbenzene	41247	1830	not found		≫99,9
hexylbenzene	26725	1208	726	43	97.3

Table 3. continued

compound	raw effluent		demulsified effluent		reduction (%)
	$\bar{A}_1$[a] (n = 3),	s[b] (pA*s)	$\bar{A}_1$[a] (n = 3)	s[b] (pA*s)	
		Cycloalkanes			
methylcyclohexane	**5419**	*216*	**not found**		**≫99,9**
3,5-dimethylcyclohexane	**7569**	*319*	**not found**		**≫99,9**
1,1,3-trimethylcyclohexane	**11476**	*548*	**not found**		**≫99,9**
1,2-dimethyl-3-(1-methylethyl)cyclopropane	**8142**	*366*	**not found**		**≫99,9**
1,2,3-trimethylcyclohexane	**3844**	*163*	**1535**	*76*	**60.1**
1,1,2,3-tetramethylcyclohexane	**14721**	*594*	**not found**		**≫99,9**
cyclodecane	**7499**	*336*	**not found**		**≫99,9**
2-butyl-1,1,3-trimethylcyclohexane	**47319**	*1499*	**4614**	*280*	**90.2**
cyclotridecane	**6487**	*295*	**857**	*29*	**86.8**
		Ethers			
2,5-dihydrofuran	**2485**	*105*	**1578**	*74*	**36.5**
allyl methallyl ether	**1522**	*63*	**not found**		**≫99,9**
2-methyl-2-oxazoline	**7596**	*328*	**4422**	*192*	**41.8**
2-isopropyl-2-methyloxirane	**2080**	*99*	**2057**	*102*	**1.1**
3-ethoxy-2-methylpropene	**3148**	*134*	**2990**	*136*	**5.0**
		Ketones			
2-butanone	**79053**	*3132*	**57019**	*2375*	**27.9**
3-methylbutanone	**8729**	*417*	**6985**	*345*	**20.0**
2-pentanone	**408089**	*15422*	**297377**	*11485*	**27.1**
methyl isobutyl ketone	**11146**	*409*	**3247**	*139*	**70.9**
2-methyl-3-pentanone	**3148**	*155*	**2990**	*149*	**5.0**
3-hexanone	**10777**	*415*	**10399**	*403*	**3.5**
5-methyl-2-hexanone	**4088**	*167*	**1586**	*74*	**61.2**
2-heptanone	**1296**	*66*	**760**	*39*	**41.4**
3-heptanone	**7342**	*315*	**5064**	*216*	**31.0**
cyclohexanone	**6971**	*316*	**3690**	*171*	**47.1**
5-methyl-3-heptanone	**4714**	*190*	**2336**	*111*	**50.4**
2-methylcycloheptanone	**7369**	*319*	**826**	*51*	**88.8**
acetophenone	**19924**	*740*	**7265**	*276*	**63.5**
2-nonanone	**2841**	*115*	**1287**	*65*	**54.7**
1-(4-methylphenyl)ethanone	**24748**	*972*	**2335**	*97*	**90.6**
6-methyl-2-heptanone	**10382**	*494*	**4936**	*235*	**52.5**

[a] $\bar{A}_1$ = average peak area. [b] s = standard deviation.

phase determined by the developed DHS-GC-MS procedure is listed in Table 3. Inspection of Table 3 reveals that the content of all classes of organic compounds undergoes a significant reduction. The degree of reduction in content increases with hydrophobicity of chemical compounds present in the effluents. The highest effectiveness of reduction in content was achieved for alkanes, cycloalkanes, and aromatic compounds. In the remaining groups of organic compounds the effectiveness of reduction in content increases with the length of alkyl chain.

3.2. Identification and Distribution of VSC Concentrations in the Effluent Headspace. Mirror image SHS-GC-PFPD chromatograms of the headspace of raw postoxidative effluent and the effluent from which organic phase was removed are shown in Figure 4.

The concentrations of identified and approximate concentrations of unidentified volatile sulfur compounds in the headspace of raw postoxidative effluent and the demulsified effluent are compared in Table 4. Twenty-four volatile sulfur compounds were identified in the headspace and the chromatogram contained over 50 other VSCs. The compounds are formed during thermal cracking of high molecular weight sulfur compounds occurring in the vacuum residue undergoing oxidation. A fraction of VSCs is oxidized during bitumen production. Their presence in the effluents results mainly from the high volatility of VSCs which, under conditions of bitumen oxidation, are mostly removed from the bitumen mass with hot air and steam. Washing with an aqueous solution of sodium hydroxide assures nearly quantitative absorption of acidic VSCs. Their retention is based on chemical absorption with the formation of respective organic sulfides. Their release from the effluent can only take place if effluent pH is lowered.[17] Under conditions used for the SHS-GC-PFPD analyses, the headspace–alkaline solution equilibrium is strongly shifted toward the ionized form.

The data shown in Table 4 reveal that a substantial reduction in content of some VSCs is possible during the first postoxidative effluent pretreatment stage, i.e., demulsification as a way of removing the organic phase. A decrease in VSC content in the effluent is desirable due to their malodorousness, which can be experienced during their release to the atmosphere at successive stages of treatment in a wastewater treatment plant. These stages are generally carried out in open tanks, in which separation of the organic phase is accomplished through flotation, flocculation, and biological treatment.

3.3. Identification and Distribution of VNC Concentrations in the Effluent Headspace. Static headspace and gas chromatography with nitrogen–phosphorus detector (SHS-GC-NPD) chromatograms of raw postoxidative effluents and

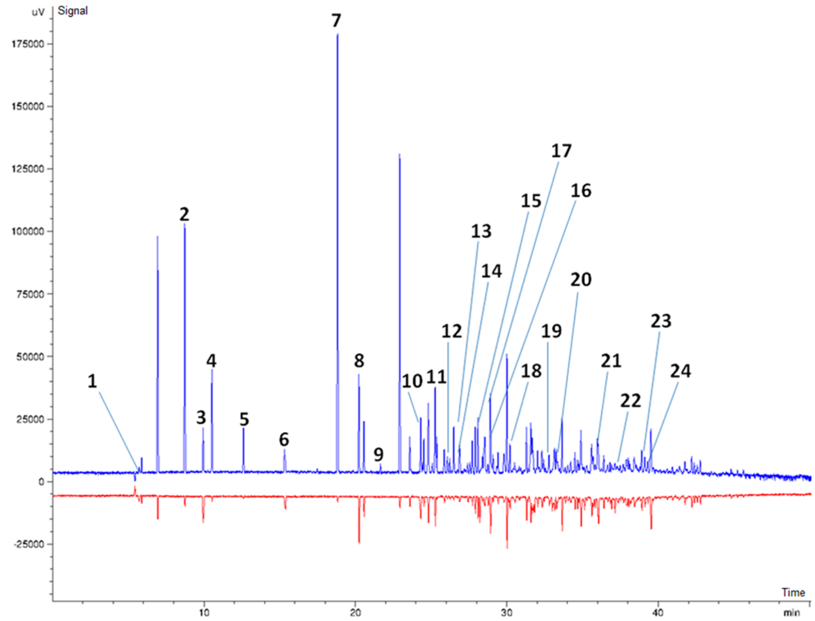

Figure 4. Mirror image SHS-GC-PFPD chromatograms of raw postoxidative effluent (blue) and the effluent from which organic phase was removed (red). Identified compounds: (1) hydrogen sulfide; (2) ethanethiol; (3) carbon disulfide; (4) 2-propanethiol; (5) 1- propanethiol; (6) thiophene; (7) dimethyl disulfide; (8) 3-methyl-1-butanethiol; (9) 3-methylthiophene; (10) 2-ethylthiophene; (11) dipropyl sulfide; (12) diethyl disulfide; (13) 1-hexanethiol; (14) 1,3-propanedithiol; (15) thiophenol; (16) 1,4-butanedithiol; (17) di-*tert*-butyl sulfide; (18) 1-heptanethiol; (19) dibutyl sulfide; (20) dipropyl disulfide; (21) benzothiophene; (22) 1-nonanethiol; (23) dihexyl sulfide; (24) 1-decanethiol.

Table 4. Comparison of Headspace Concentrations of Volatile Sulfur Compounds of Raw Postoxidative Effluent and Demulsified Effluent

	raw postoxidative effluent			demulsified effluent			
compound	$\bar{C}_1$[a] (μg/m^3; $n = 3$)	s[b] (μg/m^3)	recalcd headspace concn expressed as mole fraction (ppb)	$\bar{C}_1$[a] (μg/m^3; $n = 3$)	s[b] (μg/m^3)	recalcd headspace concn expressed as mole fraction (ppb)	reduction (%)
hydrogen sulfide	**94.8**	*4.1*	71.8	**89.2**	*3.6*	67.6	**5.9**
ethanethiol	**385.0**	*13.3*	291.7	**45.1**	*1.7*	34.1	**88.3**
carbon disulfide	**94.0**	*3.6*	71.2	**89.0**	*3.7*	67.4	**5.3**
2-propanethiol	**171.4**	*5.2*	129.9	**33.1**	*1.3*	25.1	**80.7**
1-propanethiol	**93.6**	*3.8*	70.9	<LOQ			**94.3**[c]
thiophene	**90.1**	*3.8*	68.3	**28.3**	*1.1*	21.5	**68.6**
dimethyl disulfide	**695.5**	*23.0*	527.1	**34.9**	*1.5*	26.5	**95.0**
3-methyl-1-butanethiol	**107.1**	*4.2*	81.2	**71.0**	*2.8*	53.8	**33.7**
3-methylthiophene	**23.6**	*1.2*	17.8	**23.2**	*0.9*	17.6	**1.5**
2-ethylthiophene	**100.7**	*4.3*	76.3	**99.6**	*4.5*	75.5	**1.1**
dipropyl sulfide	**153.1**	*5.9*	116.0	<LOQ			**92.5**[c]
diethyl disulfide	**39.6**	*1.5*	30.0	**25.4**	*1.0*	19.3	**35.9**
1-hexanethiol	**95.9**	*4.6*	72.7	**37.7**	*1.6*	28.6	**60.7**
1,3-propanedithiol	**25.9**	*1.3*	19.7	<LOQ			**66.6**[c]
thiophenol	**88.5**	*3.8*	67.1	**69.1**	*1.9*	52.4	**21.9**
1,4-butanedithiol	**126.6**	*5.0*	95.9	**24.3**	*1.0*	18.4	**80.8**
di-*tert*-butyl sulfide	**188.1**	*7.5*	142.5	**101.7**	*5.3*	77.1	**45.9**
1-heptanethiol	**69.0**	*3.1*	52.3	**47.9**	*2.2*	36.3	**30.6**
dibutyl sulfide	**32.4**	*1.4*	24.5	**31.1**	*1.4*	23.5	**4.0**
dipropyl disulfide	**60.9**	*2.3*	46.2	**60.1**	*2.4*	45.5	**1.4**
benzotiophene	**60.1**	*2.5*	45.5	**59.4**	*1.9*	45.0	**1.0**
1-nonanethiol	**50.2**	*1.8*	38.0	<LOQ			**82.4**[c]
dihexyl sulfide	**66.4**	*3.2*	50.3	**53.2**	*2.0*	40.3	**20.0**
1-decanothiol	**17.7**	*1.0*	13.4	<LOQ			**65.6**[c]
sum of identified VSCs	**2930**	*111*	2221	**1064**	*42*	806	**63.7**
sum of unidentified VSCs	**5813**	*273*	4405	**4645**	*202*	3520	**25.0**

[a] $\bar{C}_i$ = average headspace concentration. [b] s = standard deviation. [c] Difference calculated on the basis of the value in the interval LOD < X < LOQ.

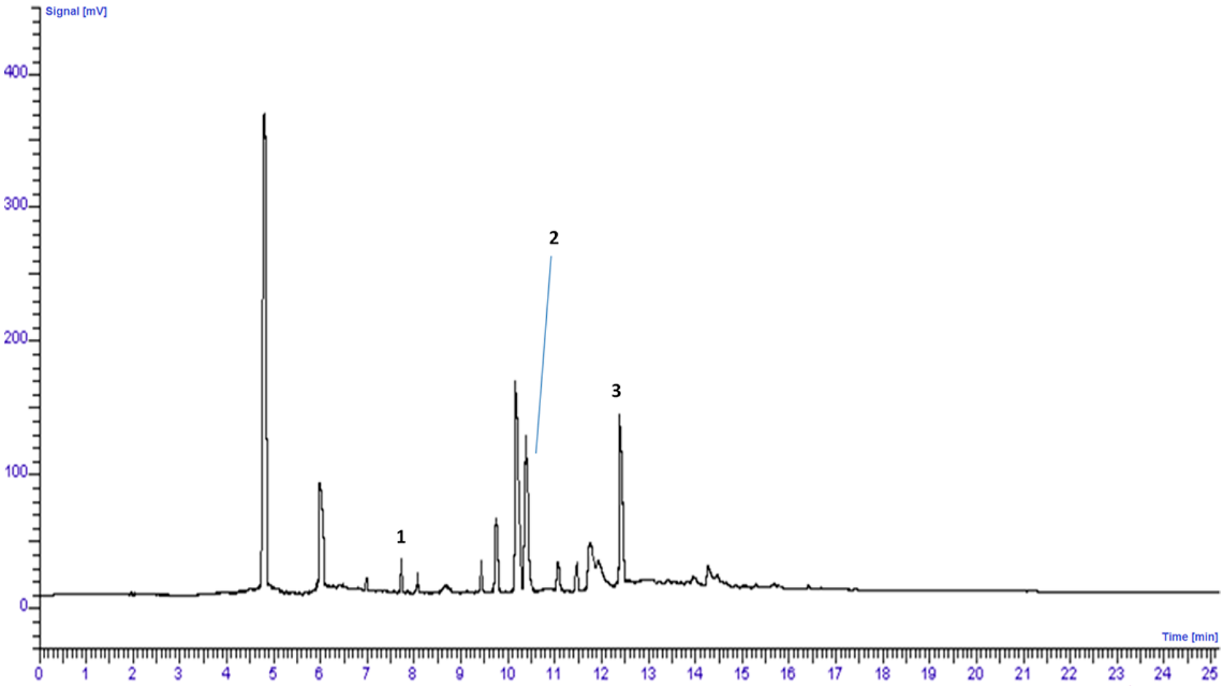

Figure 5. SHS-GC-NPD chromatogram of raw postoxidative effluent. Identified compounds: (1) pyridine; (2) 2-methylpyridine; (3) 2,4-dimethylpyridine.

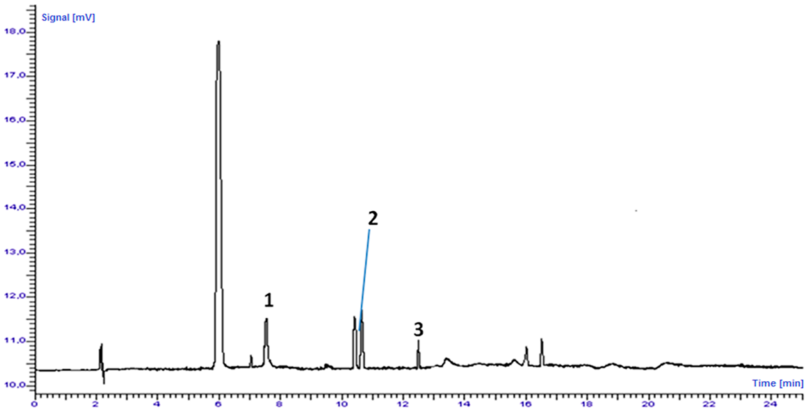

Figure 6. SHS-GC-NPD chromatogram of postoxidative effluent following demulsification. Compound identification as in Figure 5.

Table 5. Comparison of Headspace Concentrations of Volatile Nitrogen Compounds of Raw Postoxidative Effluent and Demulsified Effluent

	raw postoxidative effluent			demulsified effluent			
compound	$\overline{C}_1$[a] (mg/m^3; *n* = 3)[a] (*n* = 3)	*s*[b] (mg/m^3)	recalcd headspace concn expressed as mole fraction (ppm)	$\overline{C}_1$[a] (mg/m^3; *n* = 3)[a] (*n* = 3)	*s*[b] (mg/m^3)	recalcd headspace concn expressed as mole fraction (ppm)	reduction (%)
pyridine	**16.22**	*0.68*	4.96	**5.21**	*0.17*	1.59	**67.9**
2-methylpyridine	**23.12**	*0.93*	6.01	**6.12**	*0.25*	1.59	**73.5**
2,4-dimethylpyridine	**29.87**	*1.10*	6.76	**5.20**	*0.20*	1.18	**82.6**
sum of unidentified VNCs (as pyridine)	**89.12**	*5.81*	27.24	**13.10**	*0.84*	4.00	**85.3**

[a] $\overline{C}_1$ = average headspace concentration. [b] *s* = standard deviation.

demulsified effluents are shown in Figures 5 and 6, respectively. Similarly to volatile sulfur compounds, a much richer composition of the headspace compared to bitumen samples was observed.

A comparison of headspace concentrations of volatile nitrogen compounds of raw postoxidative effluent and demulsified effluent is shown in Table 5.

The removal of organic phase from the effluents results in a substantial decrease in concentration of volatile nitrogen compounds in the effluents. The reduction in content of individual VNCs by 68−85% results in a much lighter load of organic contaminants passed with the wastewater to a treatment plant. This lowers the cost and time required to effectively treat wastewater and also lowers biotoxicity of the effluent toward the activated sludge.

3.4. Changes in Total VOC Content in the Effluent Headspace. The developed procedure enables a rapid and accurate determination of changes in the VOC content in the effluents. Chromatographic conditions used ensure complete elution of volatile organic compounds in several minutes. Chemical compounds present in a sample are eluted from the chromatographic column as one peak. The investigations carried out during validation of the procedure demonstrate that such a solution, despite its simplicity, ensures accurate results. When separation conditions are changed, an identical chromatographic system can be used to examine the boiling point distribution of sample components using empty column gas chromatography (EC-GC).[36,37] Changes in total VOC content in the effluent headspace resulting from the removal of organic phase can be treated as a general measure of the effectiveness of reduction of VOC content in the effluents. The total VOC content in the headspace of the investigated bituminous materials is listed in Table 6. The changes of COD and BOD as well as toxicity of the effluents are listed in Table 7.

Table 6. Compilation of Total VOC Content in the Headspace of Bituminous Materials Determined Using SHS-GC-FID

raw postoxidative effluent			effluent after removal of organic phase			
$\bar{C}_1$[a] (n = 3; mg/m^3)	s[b] (mg/m^3)	recalcd head-space concn expressed as mole fraction (ppm)	$\bar{C}_1$[a] (n = 3; mg/m^3)	s[b] (mg/m^3)	recalcd head-space concn expressed as mole fraction (ppm)	reduction in content
5384	*205*	8227	**1786**	*71*	2729	**66.8%**

[a] $\bar{C}_1$ = average headspace concentration. [b] s = standard deviation.

Table 7. Comparison of Changes in Monitored Effluent Parameters Resulting from Removal of Organic Phase

	raw effluent		demulsified effluent		
parameter	av value (n = 3)	s[a]	v value (n = 3)	s[a]	change (%)
COD (mgO$_2$/dm^3)	**11990**	*803*	**4720**	*325*	61
BOD$_5$ (mgO$_2$/dm^3)	**6620**	*470*	**2075**	*145*	69
acute toxicity (%)					
EC$_{20}$	**0.10**		**0.20**		50
EC$_{50}$	**0.40**		**0.80**		50

[a] s = standard deviation.

The changes in total VOC content in postoxidative effluents resulting from the removal of organic phase were comparable to the change in VNC content. Both for VNCs and for VOCs the reduction in content increases with the hydrophobic nature of individual chemical compounds, as their content in raw postoxidative effluents is determined by the organic phase−aqueous phase partition coefficient.

To supplement the above results of changes in VOC content in the effluents resulting from the removal of organic, the changes in other quality parameters describing the load and nature of pollutants present in postoxidative effluents are discussed below.

The above results reveal that a technically simple effluent demulsification results in a substantial reduction in pollutant content. BOD and COD values are reduced by more than 60%. The reduction in total VOC content in the effluents is of a similar magnitude. For strongly hydrophobic compounds this degree of reduction is close to 100% in the majority of cases. The developed procedures of determination of the effluent headspace composition allow a substantial extension of wastewater quality parameters to include the VOC content. Universal applicability to wastewater treatment processes is an advantage of the developed procedures. Identical procedures can be successfully used in the investigation of effectiveness and transformations taking place during advanced processes of effluent oxidation.

4. CONCLUSION

Alkaline effluents from the bitumen production are characterized by a complex composition. In their raw form the effluents are strongly emulsified. The presence of an emulsified organic phase in the aqueous phase of the effluents results in their high toxicity toward the activated sludge of a wastewater treatment plant as well as malodorousness. One hundred and fourteen volatile organic compounds were identified in the raw postoxidative effluents. Analysis of the results revealed that over 400 volatile organic compounds were present in the effluent headspace. If chromatographic resolution were improved, e.g., by using a two-dimensional separation or preliminary fractionation, this number would likely be greater.

The procedures described in this work enable detailed identification of VOCs and determination of distribution of concentration of individual classes of chemical compounds. The determination of changes in concentration of individual classes of VOCs, including malodorous volatile sulfur compounds, and changes in total VOC content expands considerably the number of data on wastewater treatment processes.

The method of preliminary wastewater treatment, involving the removal of organic phase through effluent demulsification, discussed in this work allows a substantial reduction of the total pollutant load accompanied by a proportional reduction in VOC content.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure showing DHS-GC-MS chromatogram of raw postoxidative effluent. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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