Process Control and Investigation of Oxidation Kinetics of Postoxidative Effluents Using Gas Chromatography with Pulsed Flame Photometric Detection (GC-PFPD)

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This article presents the results of investigations on the use of headspace analysis and gas chromatography with pulsed flame photometric detection (HSA-GC-PFPD) to evaluate the effectiveness of oxidation of postoxidative effluents from the production of bitumens. Samples of effluents from the bitumen oxidation unit were used in the experiments. In addition, the kinetics of effluent oxidation was also investigated. The content of volatile sulfur compounds (VSCs) was determined using HSA-GC-PFPD. The results were correlated with chemical oxygen demand (COD). The changes in concentration of individual volatile sulfur compounds in the course of effluent oxidation were measured, which enabled the determination of the order of the oxidation reactions. The usefulness of the determination of VSCs in the headspace as a reliable technique for evaluating the reduction in emissions of volatile malodorous compounds was demonstrated. The developed method is also useful for process control of the oxidation of postoxidative effluents. The procedure ensures an objective evaluation of the effectiveness of the removal of volatile sulfur compounds from postoxidative effluents. The experimental results revealed that the effectiveness of the oxidation of organosulfur compounds was much higher than that of other classes of organic compounds. Furthermore, the order of oxidation reactions along with the rate constants of thiophenol, *p*-thiocresol, and hydrogen sulfide were determined. An advantage of the developed procedure is that it can be automated.

1. Introduction

Increasingly stringent environmental regulations have resulted in strict requirements regarding water/wastewater policies in the chemical, petrochemical, and related industries. Minimization of the effects of industrial activities on the environment can be accomplished by limiting emissions of chemical compounds (mainly organics) to the atmosphere, among other methods. The problem involves both primary ecotoxicity of the emitted volatile organic compounds (VOCs) and their further conversions resulting in the formation of environmentally hazardous compounds. At the same time, the emitted compounds are often malodorous. The main approaches to limiting atmospheric emissions are based on the encapsulation of technological processes and fume removal through air extraction, followed by further neutralization using a variety of operations.[1−13] Such processes often result in the formation of effluents, which should be subjected to further treatment to reduce their toxicity and malodorousness. Analytical procedures determining the effectiveness of VOC removal processes and quantifying their emissions to the atmosphere play an important role in such efforts.[16−21]

Gas chromatography is often used to examine emissions of volatile organic compounds.[22−30,37] To enable the objective evaluation of malodorousness, analytical procedures should aim at the determination of volatile organic compounds containing nitrogen and sulfur.[46] Devices based on a set of sensors, so-called electronic noses, are increasingly used in these studies.[33−36]

1.1. Generation and Characteristics of Effluents Formed during Production of Bitumens. The most common method of bitumen production is oxidation of the bottoms with hot air, sometimes blending with so-called propane or pentane asphalt, as well as with the extracts from deasphalting. The bottoms are fed at 170−180 °C at the top of the reactor. Air is blown countercurrently or by using a set of turbines. The bitumen produced is removed at the bottom of the reactor. The waste gases formed during the process are cleaned in a scrubber and passed to a combustion furnace.

Both during vacuum distillation of crude oil and in the bottoms oxidation reactor of the bitumen production unit, thermal cracking takes place to a varying extent as a result of overheating of the starting material on the surface of heating elements. Unsaturated hydrocarbons (olefins) are formed first. The olefins undergo further conversions, including condensation, addition to double bonds, and oxidation, that result in the formation of a wide variety of organic compounds, primarily ketones and aldehydes, as well as organosulfur compounds, polycyclic aromatic hydrocarbons (PAHs), and others. The majority of aldehydes are rapidly oxidized to carboxylic acids. A large fraction of volatile chemical compounds formed in this manner is removed during scrubbing of waste gases. However, a small amount of volatiles remains dissolved in bitumen. The presence of such byproducts formed during bitumen production in the postoxidative effluent presents a considerable problem, mostly because of an unpleasant odor and a high degree of ecotoxicity. They are emitted not only from the effluent from a bitumen oxidation unit but also during filling of tanks with bitumen.

As a result of the biotoxicity and high malodorousness of the effluents, there is a need for their preliminary cleanup prior to sending to a wastewater treatment plant. This, in turn, requires the availability of an effective technology for effluent pretreatment, ensuring a significant reduction of malodorousness and biotoxicity.

This work describes the possibility of using pulse flame photometric detection coupled with capillary gas chromatog-

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raphy and headspace analysis (HS-GC-PFPD) to evaluate the degree of emission reduction of volatile organosulfur compounds as a control procedure for waste treating technology from a bitumen oxidation unit. In addition, a correlation between the effectiveness of oxidation of volatile organosulfur compounds and chemical oxygen demand (COD) was also examined.

2. Materials and Methods

2.1. Materials. The materials used in this work are compiled in Table S1 (see the Supporting Information).

2.2. Samples and Their Characteristics. Effluents generated in the bitumen oxidation process in the refinery of the LOTOS Group, Inc. (Gdansk, Poland) were used in this study. The effluents (aqueous phase, pH ∼12) contained about 1% of a strongly emulsified organic phase. In separate studies, outside the scope of this article, the following compounds other than saturated hydrocarbons were identified in the headspace above the effluents using gas chromatography with mass spectrometry (GC-MS): alcohols, namely, ethanol, 1-propanol, 2-butanol, 1-butanol, 2-pentanol, 1-pentanol, 2,2-dimethyl-1,3-propanediol, cyclohexanol, and 1-hexanol; ketones, namely, acetone, 2-butanone, 2-pentanone, 3-pentanone, 3-hexanone, 2-hexanone, 4-methyl-2-hexanone, 2-heptanone, 3-methylcyclohexanone, and 6-methyl-2-heptanone; aldehydes, namely, acetaldehyde, benzyl aldehyde, and 2-hexenal; and *p*-xylene.

2.3. Instrumentation. Gas Chromatography. Gas chromatography was performed using an Agilent model 6890 gas chromatograph (Agilent, Foster City, CA) with a model 5380 PFPD detector (OI Analytical) and a 60 m × 0.32 mm ×1.0 μm HP1 GC capillary column (Agilent).

Chemical Oxygen Demand. A Merck SQ 118 spectrophotometer (Merck, Darmstadt, Germany) and Spectroquant test kits for COD (Merck) were used for COD measurements.

Oxidation Potential Measurements. Oxidation potential measurements were performed using a platinum electrode (Metron, Turon, Poland), a saturated calomel electrode (Metron), a salt bridge filled with the saturated KCl solution, a reference cell with the saturated KCl solution (50 mL), a titration cell (50 mL), a magnetic stirrer, a 20-mL buret, and a model 5170 pH meter (Elwro, Wroclaw, Poland).

Oxidation of Effluents. The homemade reaction chamber is shown in Photograph S1 and Figure S1 of the Supporting Information. It consists of the following modules: a pressure reactor made of acid-resistant steel (volume ≈ 2.5 L) with an electromagnetic safety valve, the maximum allowed pressure within which was 20 bar;a model 06463 plunger pump made of acid-resistant steel (WZDZ, Opole, Poland); a magnetic stirrer; and a tank with compressed air and a pressure regulator.

2.4. Procedures. 2.4.1. Preparation of Standard Solutions. A number of standard solutions of sulfur compounds were prepared in *n*-pentane. Stock solutions were made by adding 1 μL of individual sulfur compounds using a microsyringe to 10 mL of *n*-pentane in a volumetric flask. Standard solutions of solid standards were prepared by dissolving weighed amounts of the standards (ca. 10 mg). Next, the solutions were diluted to obtain the final concentrations of sulfur compounds at a 10 ppm level. Because of their negligible solubilities in pentane, solutions of diethyl sulfone and *p*-thiocresol were prepared in methanol. Standard solutions were introduced onto the GC capillary column in a split mode (100:1). The injection volume was 0.2 μL.

A standard mixture of hydrogen sulfide in nitrogen was introduced from a tank into a Tedlar bag. Subsequent standard mixtures were prepared by successive dilutions with high-purity nitrogen of the initial standard mixture in Tedlar bags. The mixture was introduced into the GC using a gastight syringe in a splitless and split mode (10:1). Calibration was performed taking into consideration that the PFPD response to sulfur varies with the square of the concentration (the square root of the response was plotted against concentration).

2.4.2. Effluent Oxidation. A volume of 2 L of the effluent was placed in the reactor with the stirrer. A perhydrol (30% hydrogen peroxide) solution was fed to the reactor (140 mL of perhydrol per 2 L of effluent) through a tube placed in the reactor cover at a flow rate of about 30 mL/min (the ratio of oxidant mass expressed as oxygen to COD was about 0.41 [(g of O_2)/∑COD]. The process was carried out at 150 °C. After the desired temperature had been reached, the pressure in the reactor was increased to 10 bar using air from a compressed air tank. The oxidation was carried out for 180 min. During oxidation, 10-mL samples of the solution were collected through a pipe having an inlet in the cover but extending to the lower part of the reactor. To terminate the oxidation reaction, a 1 M Na_2SO_3 solution was added to samples in an amount ensuring a zero value of the oxidation potential.

2.4.3. Headspace Analysis. A 10-mL sample of the effluent was placed in a 15-mL vial provided with a poly(tetrafluoroethylene)- (PTFE-) lined silicone septum. The sample was thermostatted for 1 h at 80 °C. A 0.2-mL headspace sample was injected using a gastight syringe.

2.4.4. Chromatographic Conditions. The chromatographic conditions were injection mode, split 10:1; injector temperature, 300 °C; and carrier-gas flow rate, 1.2 mL/min. The GC oven temperature was programmed as follows: hold at 40 °C for 7 min, increase to 260 °C at 5°/min, increase to 300 °C at 30°/min, and hold at 300 °C for 5 min.

2.4.5. Operating Parameters of PFPD. The PFPD operating parameters were as follows: photomultiplier tube (PMT) voltage, 600 V; range, 10 μA/V; igniter current, 3.1 A; detector temperature, 220 °C; PFPD pulse rate, 3.57 Hz; gate wide, 6−24 ms. The combustion chamber mixture consisted of 21.0 psig hydrogen, 12.6 psig air1; makeup gas: 14.8 psig air2.

2.4.6. Determination of COD. Effluent samples were oxidized with a hot solution of potassium dichromate in sulfuric acid using a silver catalyst. Chlorides were masked with mercury(I) sulfate. The concentration of excess dichromate ions was determined photometrically.

2.5. Quality Assurance of Data. The limit of detection (LOD) (signal-to-noise ratio S/N = 3) and linear dynamic range of the PFPD detector were determined for each of the standard mixtures of sulfur compounds. The limit of quantitation (LOQ) was taken as twice the limit of detection (S/N = 6). All of the characteristics were determined for the conditions of headspace analysis of effluent samples, with a sampling volume of 0.2 mL and chromatographic conditions as described in section 2.4.4 and 2.4.5.

As a result of the physical form of standards used in this work (hydrogen sulfide as a gas mixture and other standards as liquid solutions), absolute LOD values, expressed in picograms, were determined directly for all standards. For hydrogen sulfide, the LOD was also determined directly as molar concentration of the analyte in the gas phase (nmoles of H_2S per mole) in ppb. For the remaining standards, LOD in ppb was estimated for the analytical conditions of headspace analysis using the ideal gas equation.

The linear dynamic range for the PFPD detector was determined individually for each standard by injecting standard solutions with increasing volatile sulfur compound (VSC)

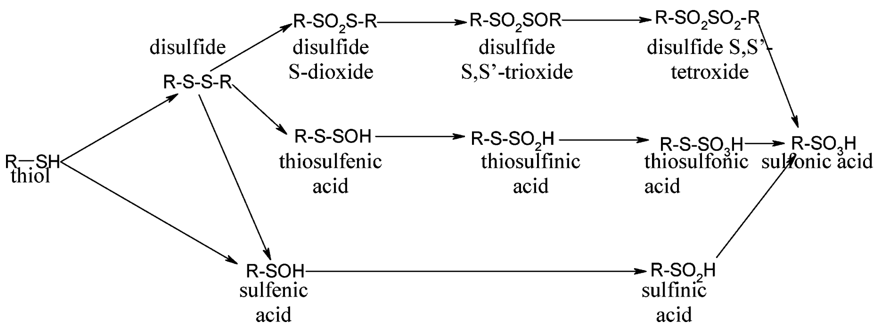

Figure 1. Oxidation pathways of thiols.[32]

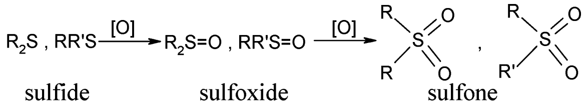

Figure 2. Oxidation pathways of sulfides.[14,15]

content. The LOQ value (expressed in picomoles of sulfur) was taken as the lower limit of linearity, whereas the upper limit was assumed to be the amount of standard for which the response factor value deviated from the average response factor (R_f). The limit of deviation for a given standard was taken as twice the relative standard deviation (RSD) of the average response for this standard.

3. Results and Discussion

3.1. Main Pathways of Oxidation of Organosulfur Compounds. Depending on the reaction conditions and the nature of organosulfur compounds, several main pathways of oxidation reaction are possible.[14,15,32]

As shown in Figures 1 and 2, the final oxidation products of thiols or disulfides are sulfonic acids (Figure 1), whereas the oxidation of sulfides yields sulfones (Figure 2).

In both cases, the reaction products are characterized by a negligible volatility compared with the reactants. Thus, to reduce emissions of volatile sulfur compounds from effluents, waste treatment should be carried out in such a way as to result in the formation of low volatility and, ultimately, nonvolatile derivatives (i.e. sulfones and sulfonic acids).

3.2. Evaluation of the Developed Oxidation Method. Chromatograms of the headspace over an effluent sample before (lower chromatogram) and after (upper chromatogram) the oxidation are shown in Figure 3.

Retention times for individual standards of volatile sulfur compounds are listed in Table S2 (see the Supporting Information), and average values of the response factor of PFPD for the investigated sulfur compounds are compiled in Table S3 (Supporting Information).

An advantage of PFPD is its almost equimolar response to sulfur.[38−40] This enables an accurate determination of the total amount of sulfur compounds in a sample based on calibration using just one standard compound or based on the average value of the response factor. The average response factor, R_f, was calculated from the response factors of individual sulfur compounds. The R_f values for hydrogen sulfide and dithiols were excluded from the calculation because of their large deviations from the average response factor. The response factors for dibenzothiophene and its derivatives were also excluded, because the retention times for these compounds under the chromatographic conditions used exceeded 50 min and no peaks with retention times above 48 min were found in chromatograms of the investigated effluent samples.

The average response factor determined in this manner could be used for a relatively accurate determination of unidentified sulfur compounds in the headspace over the effluents.

The numerical value of the average response factor was 152356 μV s/(pmol of S) with a relative standard deviation of 9.1%.

Because the smallest value of the response factor was found for hydrogen sulfide and the gaseous form of its standard solution, the LOD and LOQ values determined for this compound are most representative of the sensitivity of the procedure used in this work. The results of some earlier works on the determination of VSCs[42] also indicated that the LOD values expressed as the absolute mass of sulfur were, on average, 5−10 pg higher for hydrogen sulfide than for other volatile sulfur compounds, for which the absolute LOD expressed as the mass of sulfur was about several picograms (splitless introduction of gas samples). The problems with the determination of hydrogen sulfide result primarily from its reactivity and adsorption on the surface with which it is in contact[41] (syringe and equipment).

The limit of detection (LOD) of sulfur in volatile organosulfur compounds was found to be 1.7 pg of sulfur (0.053 pmol of H_2S, 6.1 ppb) ($S/N = 3$), whereas the limit of quantitation (LOQ) was estimated at 3.4 pg of sulfur (0.106 pmol of H_2S) ($S/N = 6$). These values were determined in splitless injection mode to estimate the optimum operating parameters of the PFPD detector.

LOD values and the linear dynamic range for the PFPD detector, determined for headspace analysis of effluents (injection, split 10:1; sample volume, 0.2 mL) are compiled in Table S4 (Supporting Information). The LOD values expressed as sulfur ranged from 10.45 pg of S [0.33 pmol of S, 19.91 nmol of compound/mol of gas phase (ppb)] for di-*tert*-butyl disulfide to 16.0 pg of S (0.50 pmol of S, 61.12 ppb) for hydrogen sulfide.

Changes and percentage decreases in the concentrations of the 20 identified volatile sulfur compounds in the headspace over samples of the raw effluent (prior to oxidation) are compiled in Table 1. To determine the total VSC content in the effluent headspace, the contents of the identified VSCs were expressed as picomoles of sulfur per milliliter of headspace. This approach allows the approximate determination of unidentified VSCs on the basis of the average response factor of the PFPD detector and addition of these amounts to the total content of identified compounds. In addition, the content of identified VSCs in Table 1 is also expressed as the mole ratio in the gas phase [i.e., micromoles of compound per mole of headspace (ppm).

The obtained results (Table 1) reveal a relatively high primary VSC content in the effluents. The total VSC content in the effluent headspace prior to oxidation expressed as sulfur was 3128.6 pmol of S/mL of headspace, including 1951 pmol of

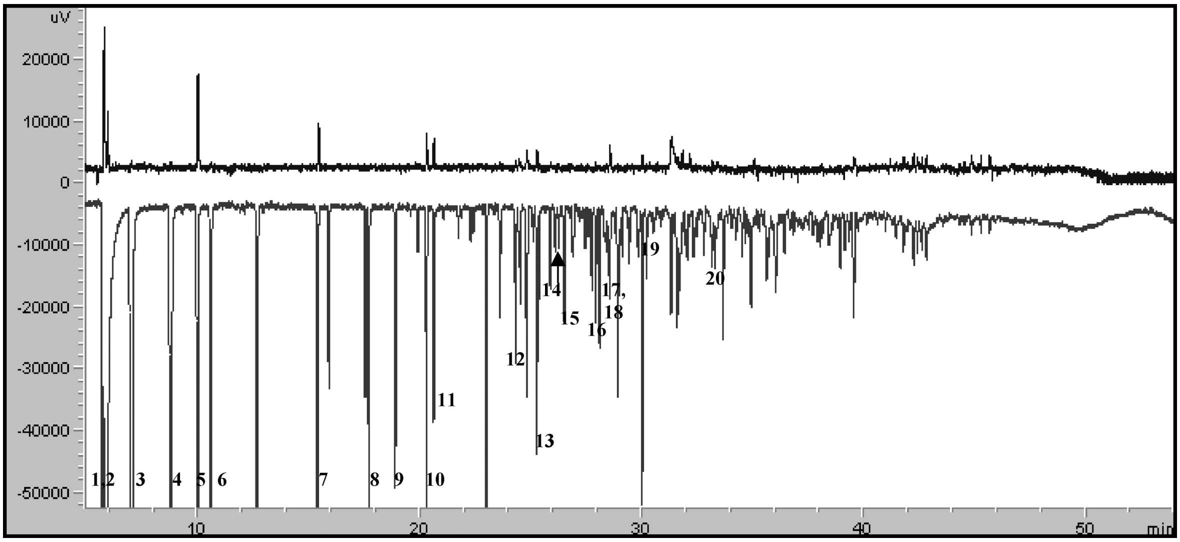

Figure 3. Mirror image HSA-GC-PFPD chromatograms of postoxidative effluent before (lower trace) and after (upper trace) oxidation. Identification: (1) hydrogen sulfide, (2) COS, (3) methanethiol, (4) ethanethiol, (5) carbon disulfide, (6) 2-propanethiol, (7) thiophene, (8) 1-buthanethiol, (9) dimethyl disulfide, (10) 2-methylthiophene, (11) 3-methyl-1-butanethiol, (12) 2-ethylthiophene, (13) dipropyl sulfide, (14) diethyl disulfide, (15) 1-hexanethiol, (16) thiophenol, (17) 1,4-butanedithiol, (18) *p*-thiocresol, (19) benzylthiol, (20) dipropyl disulfide.

S/mL of identified volatile sulfur compounds. The latter value of identified VSCs corresponds to 1803 pmol of VSCs/mL of headspace (44.08 ppm, 133.16 mg/m^3).

As a result of low odor threshold (several to several tens of parts per billion) of volatile sulfur compounds and their unpleasant odor, their amount found in the headspace is considered large. However, it should be remembered that the analytical conditions used, namely, elevated temperature (80 °C) and equilibration of the liquid−headspace system, will not be reproduced under real conditions. For example, if effluents flow through an open tank, the concentration of VSCs in the air in the region of possible emissions to the atmosphere will certainly be lower.

The concentrations of volatile sulfur compounds at various sites where malodorous compounds are emitted are compiled in Table 2. It follows from the data in the table that, at the sites where volatile sulfur compounds are emitted, their concentrations can exceed hundreds of milligrams per cubic meter (ppm).

The plots in Figure 4 illustrate the percent changes in concentrations of volatile sulfur compounds in the headspace over effluents and COD as a function of time of oxidation. The plots were prepared for those compounds for which the headspace concentration could be determined for at least the first three sampling periods, that is, at times equal to 0, 15, and 60 min. Other identified sulfur compounds were oxidized so rapidly that, after 15 min, their headspace concentrations were below the limit of detection of the method. This implies that, during a short time of the process (15 min), a substantial reduction in the content of volatile sulfur compounds (by over 83%) is possible. This reduction in VSC content in the headspace above effluents for a number of identified compounds was to below the detection limit of the method (ranging from 19.91 to 61.12 ppb, depending on the compound). A comparison with the odor threshold[43] for VSCs (e.g., 0.41 ppb for hydrogen sulfide, 3.0 ppb for dimethyl sulfide, or 210 ppb for carbon disulfide) reveals that the degree of reduction in VSC content in the headspace makes their concentrations close to or lower than the odor threshold. Such an effectiveness of the applied oxidation method can certainly be achieved for sulfur compounds with a higher molar mass, for which the odor threshold values are higher.

The results compiled in Table 1 indicate that the oxidation method used allows a substantial reduction to be accomplished in the content of mostly low-molar-mass VSCs, characterized by the lowest odor threshold values and the most unpleasant odors (methanethiol, ethanethiol, 2-propanethiol). Aromatic sulfur compounds (thiophenol, *p*-thiocresol, thiophene, 2-methyltiophene) and hydrogen sulfide are less susceptible to oxidation. Thiophenol was least susceptible to oxidation (reduction in content by 34% and 86.6% after 15 and 180 min, respectively). A degree of reduction in content of over 90% was achieved for the remaining sulfur compounds. The content of identified volatile sulfur compounds was 173.35 pmol of VSCs/mL of headspace (4.24 ppm) and 19.32 pmol of VSCs/mL of headspace (0.47 ppm) after 15 and 180 min, respectively, and the total reduction in content of VSCs was 83.47% and 98.95% respectively.

An inspection of the plots in Figure 4 reveals that the sulfur compounds are oxidized very rapidly during the initial phase of oxidation (highest concentration of perhydrol). The rate of conversion of sulfur compounds decreases substantially after 60 min of the oxidation process. The same trend is observed for COD.

The values of the correlation coefficient for the plots in Figure 4 are listed in Table 3. It follows from the data in Table 3 that the largest values of linear correlation coefficient between concentration changes in the headspace and COD are for thiophenol ($R = 0.9958$), which represents a very strong correlation, and for *p*-thiocresol ($R = 0.9639$), which indicates a strong correlation. The change in total VSC content correlates with the COD change at an $R = 0.8501$ level, which indicates a medium correlation.

Oxidation of thiols can result in the formation of disulfides or sulfenic acids, which, as shown in Figure 1, depending on the oxidizing agent and reaction conditions (temperature and pH) used, can be further oxidized, eventually yielding sulfonic acids. Oxidation of thiols with oxygen in aqueous medium at pH values of 7−9 yields disulfides, whereas in strongly alkaline media (pH ca. 12), the reaction products are sulfonic acids.[47]

The data in Table 1 do not indicate any increase in disulfide concentrations. On this basis, it was concluded that the oxidation conditions used yield primarily sulfonic acids.

Table 1. Changes in Concentration of Identified Volatile Sulfur Compounds and COD during Oxidation Process

compound	concentration in the effluent headspace during the oxidation process[a] [(pmol of S)/mL] start	after 15 min	after 60 min	after 180 min	percentage decrease in headspace concentration during the oxidation process after 15 min	after 60 min	after 180 min
2-propanethiol	321.64 (7.86)	0.00	0.00	0.00	100.0	100.0	100.0
methanethiol[b]	272.59 (6.66)	6.15 (0.15)	0.00	0.00	97.7	100.0	100.0
ethanethiol	247.75 (6.06)	0.00	0.00	0.00	100.0	100.0	100.0
COS[b]	226.94 (5.55)	13.89 (0.34)	0.00	0.00	93.9	100.0	100.0
carbon disulfide	195.97 (2.40)	29.04 (0.36)	0.00	5.87 (0.07)	85.2	100.0	97.0
hydrogen sulfide	113.22 (2.77)	40.44 (0.99)	10.84 (0.27)	4.58 (0.11)	64.3	90.4	96.0
thiophene	80.08 (1.96)	17.75 (0.43)	6.26 (0.15)	4.03 (0.10)	77.8	92.2	95.0
1-butanethiol	60.85 (1.49)	0.00	0.00	0.00	100.0	100.0	100.0
2-methylthiophene	60.70 (1.48)	11.40 (0.28)	0.00	0.00	81.2	100.0	100.0
dimethyl disulfide	58.67 (0.72)	4.13 (0.05)	0.00	0.00	93.0	100.0	100.0
dipropyl sulfide	51.21 (1.25)	10.23 (0.25)	4.12 (0.10)	0.00	80.0	92.0	100.0
3-methyl-1-butanethiol	45.51 (1.11)	10.60 (0.26)	3.72 (0.09)	0.00	76.7	91.8	100.0
p-thiocresol	40.70 (1.00)	20.25 (0.50)	8.06 (0.20)	3.73 (0.09)	50.3	80.2	90.8
2-ethylthiophene	38.53 (0.94)	6.30 (0,15)	0.00	0.00	83.7	100.0	100.0
benzylthiol	36.58 (0.89)	0.00	0.00	0.00	100.0	100.0	100.0
thiophenol	30.07 (0.74)	19.75 (0.48)	9.97 (0.24)	4.04 (0.10)	34.3	66.8	86.6
1-hexanethiol	28.32 (0.69)	0.00	0.00	0.00	100.0	100.0	100.0
dipropyl disulfide	16.87 (0.21)	0.00	0.00	0.00	100.0	100.0	100.0
1,4-butanedithiol	12.78 (0.16)	0.00	0.00	0.00	100.0	100.0	100.0
diethyl disulfide	12.25 (0.15)	0.00	0.00	0.00	100.0	100.0	100.0
sum of unidentified VSCs	1177.37	327.19	21.04	10.71	72.21	98.21	99.09
total VSCs	3128.60	517.12	64.01	32.96	83.47	97.95	98.95

Decrease in Effluent COD during Oxidation Process

parameter	start	after 15 min	after 30 min	after 60 min	after 120 min	after 180 min
COD (mg of O_2/dm^3)	48120	38925	33219	26789	20000	18760
decrease in COD (%)	–	19.07	30.97	44.33	58.44	61.01

[a] Concentrations of compounds expressed in micromoles of compound per mole of headspace (ppm) are shown in parentheses. [b] Tentative identification was based on the chromatogram obtained from the Agilent database.[31]

Table 2. Comparison of Volatile Sulfur Contents Determined from Various Sources of Malodorous Compounds[a]

source/sampling site	contents of volatile sulfur compounds	method of sample collection/determination	ref
Korea, four landfill sites: Woon Jung, BangChun, Hoei Chun, No Hyung	sum of volatile sulfur compounds: 3.9−3350 mg/m^3 with 82−98% content of hydrogen sulfide	Tedlar bag sampling method, direct loop injection onto GC column, determination by GC-PFPD	41
Korea, various emission sources located within the Ban-Wall/Si-Hwa industrial complex in Ansan city, 202 individual points at 77 individual companies during 2004−2005	H_2S, mean 4171.8 μg/m^3 (median 11.96); CH_3SH, 62.23 (1.77); DMS, 194.56 (3.30); CS_2, 463.76 (43.26); DMDS, 26.83 (1.89)	Tedlar bag sampling method, direct loop injection system (high-content VSC mode, at or above 10 ppbv) or with an air server (AS)/thermal desorption (TD) unit (low-content VSC mode, at or below 10 ppbv), determination by GC-PFPD	43
Turkey, air samples collected at the deltas of polluted creeks in the city of Izmir	H_2S, 0.7−1463.5 mg/m^3; DMS, 11.8−59.2 mg/m^3; 2-propanethiol, 1.8−19.6 mg/m^3; 2-butanethiol, 1.1−12.5 mg/m^3	sampling on glass-fiber filters impregnated with mercuric acetate (for gaseous organic sulfur compounds) and coconut shell charcoal tubes (for hydrogen sulfide) with Zefluor prefilter; determination by NIOSH method 2542, GC-FPD (for thiols), and NIOSH method 6013, ion chromatography (for hydrogen sulfide)	44
Spain; (A) urban wastewater treated in constructed wetlands; (B) wastewater from the effluent of a paper recycling industry	(A) DMS, 1118−3927 μg/m^3; DMDS, 551−946 μg/m^3. (B) DMS, 8022 μg/m^3; DMDS, 734 μg/m^3	HSA-SPME-GC-MS (equilibration time of 45 min at 25 °C)	45

[a] H_2S, hydrogen sulfide; CH_3SH, methanethiol; DMS, dimethyl sulfide; CS_2, carbon disulfide; DMDS, dimethyl disulfide.

Oxidation of organic sulfides first yields sulfoxides (Figure 2). The use of a stronger oxidizer yields corresponding sulfones. No increase in concentration of dimethyl sulfoxide, the product of oxidation of dimethyl sulfide initially identified in the headspace, was observed in the course of oxidation (Table 1). It was thus concluded that, under the prevailing conditions, oxidation of dimethyl sulfide and other organic sulfides occurring in the effluent yields sulfones of low volatility.

In conclusion, a substantial decrease in the concentration of volatile sulfur compounds in the headspace over the effluent indicates that, under the experimental conditions used, the oxidation process produces sulfones and alkylsulfonic acids as the final products.

3.3. Investigation of the Order of Oxidation Reaction of Sulfur Compounds. The obtained data enabled a preliminary investigation of the kinetics of oxidation of individual sulfur compounds and an estimation of the rate constant under the applied oxidation conditions.

The reaction order was determined for hydrogen sulfide, thiophene, *p*-thiocresol, and thiophenol from the time dependence of the concentration. Using the equations describing changes in concentration against time for zeroth-, first-, and second-order reactions, the best fit was found. The results obtained (Table 4) reveal that the oxidations of hydrogen sulfide, *p*-thiocresol, and thiophenol take place according to the kinetic equation for a second-order reaction. None of the reaction orders considered corresponded to the changes in concentration of thiophene. Rate constant values for the compounds under consideration calculated from the equations for zeroth-, first-, and second-order reactions are listed in Table 4.

The results compiled in Table 4 demonstrate that the kinetics of oxidation of volatile sulfur compounds can be described by a second-order equation or by an equation of noninteger order close to second. Relative standard deviation (RSD) was used as a parameter characterizing the precision of the rate constant values. The data in Table 4 reveal that the RSD values for the rate constants of the oxidation reactions of thiophenol, *p*-thiocresol, and hydrogen sulfide were equal to 4.9%, 10.8%, and 12.4%, respectively. The data also indicate that, for thiophene, the oxidation process is best described by a second-order equation.

The four sulfur compounds singled out in Table 4 belong to different types. A relatively good agreement between the obtained reaction orders and rate constant values (0.0012−0.0022 M^{-1} s^{-1}) allows one to make the assumption that, under the oxidation conditions used in this work, the change in concentration of volatile sulfur compounds can be described by a second-order equation.

The observed decreases in COD by 61.1% and in the headspace concentration of VSCs by almost 99% during the oxidation process demonstrate the high effectiveness of the oxidation conditions used in this study.

Sulfur compounds, including nonvolatile ones, are highly susceptible to oxidation. For other classes of organic compounds except for aldehydes (i.e., for alcohols, ketones, pyridine and its derivatives, and amines), the effectiveness of oxidation under these conditions is presumably lower. High effectiveness of removal of alcohols or ketones from effluents is not as important as that of organosulfur compounds or heterocyclic organonitrogen compounds because of the lower biotoxicity of oxygen-containing organic compounds. Hence, their presence in effluents has a less negative effect on the condition of activated sludge. In addition, the malodorousness of oxygen-containing organic compounds is lower than that of sulfur compounds in the lowest

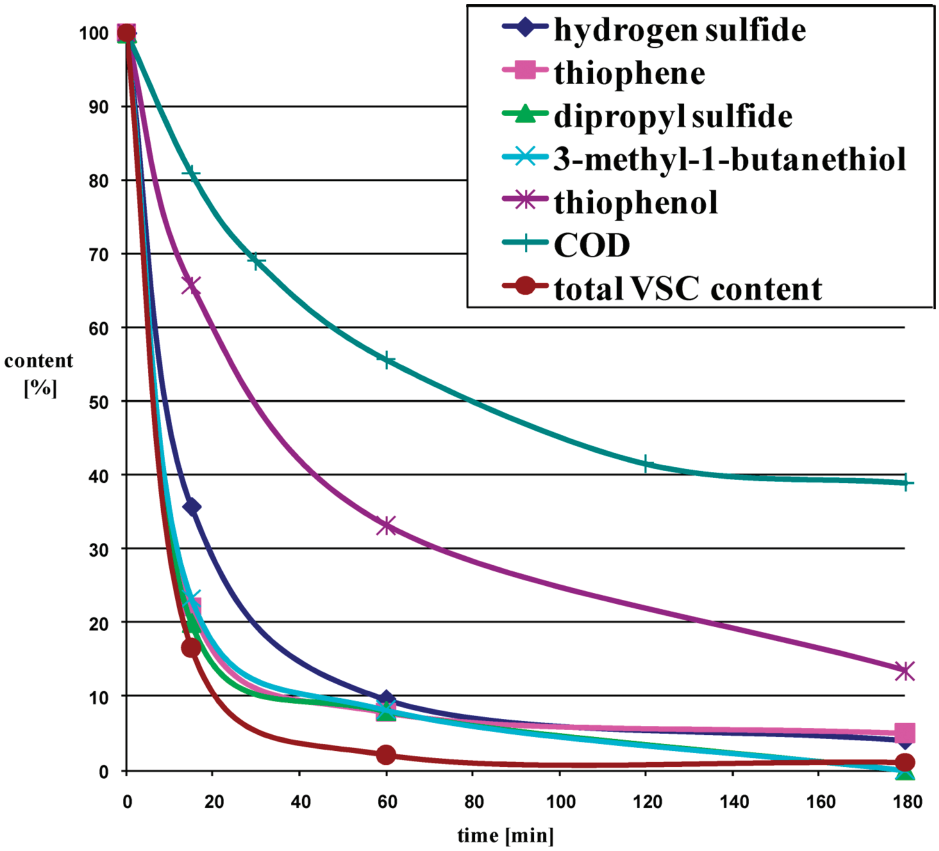

Figure 4. Changes in the chemical oxygen demand of the effluent and in the concentrations of volatile sulfur compounds in the headspace above the effluent during the oxidation process.

Table 3. Changes in VSC Concentration and COD as a Function of Time

	oxidation time (min)				
compound/parameter	0	15	60	180	R^a
hydrogen sulfide[b]	113.22 (2.77)	40.44 (0.99)	10.84 (0.27)	4.58 (0.11)	0.9249
thiophene[b]	80.08 (1.96)	17.75 (0.43)	6.26 (0.15)	4.03 (0.10)	0.8617
dipropyl sulfide[b]	51.21 (1.25)	10.23 (0.25)	4.12 (0.10)	0	0.8705
3-methyl-1-butanethiol[b]	45.51 (1.11)	10.60 (0.26)	3.72 (0.09)	0	0.8862
p-thiocresol[b]	40.70 (1.00)	20.25 (0.50)	8.06 (0.20)	3.73 (0.09)	0.9639
thiophenol[b]	30.07 (0.74)	19.75 (0.48)	9.97 (0.24)	4.04 (0.10)	0.9958
sum of identified VSCs[b]	1951.23 (44.08)	189.93 (4.24)	42.97 (1.05)	22.25 (0.47)	0.8152
sum of unidentified VSCs[b]	1177.37	327.19	21.04	10.71	0.8999
total VSC content[b]	3128.60	517.12	64.01	32.96	0.8501
COD[c]	48120	38945	26789	18760	–

[a] Correlation coefficient between concentration changes in the headspace and COD values. [b] Units of picomoles of S per milliliter (ppm). [c] Units of milligrams of O_2 per liter.

oxidation state or heterocyclic organonitrogen compounds, although it is not negligible. An investigation of the preliminary removal of organonitrogen and oxygen compounds from postoxidative effluents will be discussed in a future article.

The reduction in COD by over 61% (from 48120 to 18760 mg of O_2/dm^3) during preliminary treatment without use of a catalyst is considered to be a very good result. Such a reduction in the amount of contaminants during pretreatment protects the activated sludge of a biological waste treatment plant from being overloaded with organic compounds and allows biological treatment to degrade mostly other organic compounds that are more resistant to chemical degradation. A high degree of reduction in VSCs, and therefore in the odorousness of effluents, is an important consequence. This is particularly important in the case of open biological treatment tanks.

It should also be noted that the use of COD as a parameter characterizing the effectiveness of oxidation of malodorous volatile organosulfur compounds provides low results for the oxidation effectiveness.

4. Conclusions

In many cases, the effectiveness of waste treatment is evaluated by determining total parameters characterizing conversions taking place during oxidation process, namely, biochemical oxygen demand (BOD) and chemical oxygen demand (COD). However, for waste treatment processes aimed primarily at a reduction of malodorousness, BOD and COD do not provide a good measure of the effectiveness of these processes. In this case, techniques and procedures that can determine quantitatively the level of reduction of highly malodorous volatile organic compounds are required. The procedures used for process control in industrial laboratories should be characterized by

Table 4. Compilation of Reaction Rate Constants[a]

	thiophene		hydrogen sulfide		*p*-thiocresol		thiophenol	
time (min)	*k* (M^{-1} s^{-1})	RSD	*k* (M^{-1} s^{-1})	RSD	*k* (M^{-1} s^{-1})	RSD	*k* (M^{-1} s^{-1})	RSD
				Second-Order				
15	0.0029	37.3	0.0011	12.3	0.0017	10.8	0.0012	4.9
60	0.0025		0.0014		0.0017		0.0011	
180	0.0013		0.0012		0.0014		0.0012	
				First-Order				
15	0.1005	80.7	0.0686	61.0	0.0465	57.7	0.028	43.9
60	0.0425		0.0391		0.027		0.0184	
180	0.0166		0.0178		0.0133		0.0112	
				Zeroth-Order				
15	4.1556	101.4	4.8517	92.3	1.3634	84.5	0.6877	70.8
60	1.2303		1.7063		0.544		0.335	
180	0.4225		0.6035		0.2054		0.1446	

[a] *k* = rate constant, RSD = relative standard deviation.

simplicity of analytics, including minimization of operations related to sample preparation for analysis and amenability to automation.

The aim of this work was to develop a procedure enabling process control of emissions of highly malodorous volatile sulfur compounds with a simplified sample preparation step. At the same time, the procedure allows automation of process analytics. It enables estimation of the effectiveness of oxidation of effluents from the bitumen oxidation unit and the degree of reduction of emissions of volatile organic compounds. Gas chromatography with pulsed flame photometric detection is used to determine the degree of reduction of emissions of volatile sulfur compounds, whereas the measurement of COD provides information about the total effectiveness of the oxidation of organic compounds in the effluent.

The effectiveness of treatment of effluents from the bitumen oxidation unit subjected to oxidation in the liquid phase in an acid-resistant steel tank using perhydrol and air under elevated pressure and temperature conditions was examined. The results of this investigation lead to the following conclusions: (1) Oxidation of volatile sulfur compounds lowers their headspace concentration over the effluent by over 98%. (2) The oxidation process results in the formation of nonvolatile sulfonic acids and sulfones, which are not released to the gaseous phase, thus significantly reducing the malodorousness of the effluents. At the same time, the COD of the effluent is reduced by over 61%.

The use of HS-GC-PFPD technique enables an evaluation of the effectiveness of oxidation of malodorous volatile organosulfur compounds. It also allows the investigation of the kinetics of their oxidation.

A comparison of the results obtained by the HS-CGC-PFPD method with the COD measurements reveals that the latter technique yields low results for the effectiveness of oxidation of VOCs. However, for two analytes, namely, thiophenol and *p*-thiocresol, a strong correlation between the effectiveness of their oxidation and the change in COD value was observed. For thiophenol in particular, the correlation coefficient of 0.9958 indicates the possibility of using this compound as a universal indicator of the effectiveness of oxidation process.

The proposed HS-CGC-PFPD procedure is solvent-free and does not require any preliminary sample preparation steps prior to analysis. At the same time, it provides relatively comprehensive process information during the investigation of the effectiveness of oxidation of volatile sulfur compounds.

The developed procedure complements the existing methods of process control of waste management. The advantages discussed above, such as simplicity of determinations, allow an easy implementation in industrial laboratories. Used with an autosampler and a headspace accessory, it ensures full automation of the procedure, which is of utmost importance in industrial laboratories.

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Supporting Information Available: Detailed information about the preparation of standard solutions, determination of response factors, investigation of kinetics of effluent oxidation, and some tabulated experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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