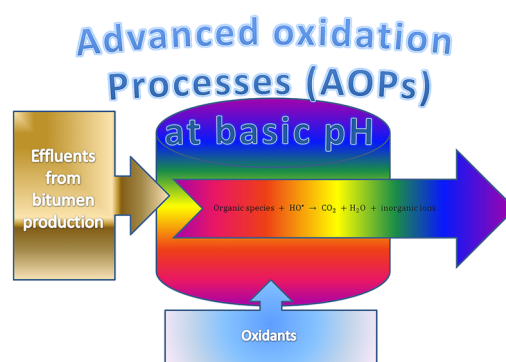


Study of Different Advanced Oxidation Processes for Wastewater Treatment from Petroleum Bitumen Production at Basic pH

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ABSTRACT: Effluents from production of petroleum bitumens were submitted to treatment by three different AOPs at basic pH (i.e., O_3 , H_2O_2 and the combination of O_3 and H_2O_2 , a so-called perozone). The paper presents studies on the identification and monitoring of the volatile organic compounds (VOCs) degradation present in the effluents and formation of byproducts, COD, BOD_5 , sulfide ions, biotoxicity, and biodegradability changes during treatment. Perozone at 25 °C with a ratio of oxidant in relation to the COD of the effluents (r_{ox}) of 0.49 achieved 43% and 34% of COD and BOD_5 reduction resulting in the most effective AOP studied. S^{2-} ions were effectively oxidized in all technologies studied. Ozonation at 25 °C and with a r_{ox} of 0.34 was the most effective process to degrade VOCs. Decrease in the biotoxicity was reported in O_3 and perozone processes. Byproduct formation in different AOPs was reported. These reductions revealed that these technologies are effective if used as pretreatment methods.



1. INTRODUCTION

Nowadays one of the most important goals in environmental technology is the minimization of the impact of effluents discharged, by reducing the levels of toxic compounds. Effluents from refinery industries contain several volatile organic compounds (VOCs) which can be easily emitted to the atmosphere causing serious danger to the environment and health.¹⁻⁵ Furthermore, they are complex and persistent to degradation and often are not degraded by biological treatments. Several technologies are available to treat and minimize the environmental impact of the effluents and one of them is the advanced oxidation processes (AOPs).

The AOP technology generates and uses mainly hydroxyl radicals (HO^\bullet) to oxidize the organic compounds.⁶⁻⁸ The HO^\bullet reacts with several types of organic compounds, producing shorter and simpler organic compounds, or in case of full mineralization, carbon dioxide (CO_2), water (H_2O), and inorganic salts if the case of chlorinated, nitrogen, sulfur compounds are present.⁷⁻⁹

One of the niches encountered in the state of the art of AOP technology is when effluents are extreme alkaline, they are often corrected to neutral/acid pH before the treatment. Effluents like post oxidative effluents from bitumen production,¹ spent caustic from gas scrubbing, petroleum sweetening and hydrocarbon washing performed in refineries,¹⁰ linear alkyl benzene¹¹ polyester, and acetate fiber dye¹² are some examples. In the case of spent caustic and post oxidative effluents, they contain a significant concentration of sulfide ions (S^{2-}), and if these effluents are corrected to neutral/acid pH, hydrogen sulfide (H_2S) is generated and can be emitted, which causes serious

consequences to the environment. In addition, these effluents contain several sulfur compounds which can be easily emitted to the atmosphere. There is a lack of studies using AOP at alkaline pH treating real effluents and also the monitoring of the organic compounds present in the effluent along with their degradation pathways.¹³ Thus, alternatives should be studied to develop AOP technology that avoid pH correction, effectively degrade the volatile organic compounds, and reduce the chemical load of pollutants. Ozone (O_3) is a powerful oxidizing agent ($E^0 = 2.07$ V) that is able to transform the organic compounds by similar pathway to the HO^\bullet .¹⁴⁻¹⁸ In basic pH, O_3 directly attacks HO^- to generate HO^\bullet .¹⁹⁻²⁴ Hydrogen peroxide (H_2O_2) is a weak acid with relatively high oxidant potential ($E^0 = 1.77$ V) which can generate hydroxyl radicals. The slow reaction rates make the process less effective when oxidizing more refractory and recalcitrant pollutants.²⁵⁻²⁷ In basic pH, the H_2O_2 reacts with HO^- to form perhydroxyl ions (HO_2^-).²⁸ It is cheap, commonly available, and it was already studied as a related AOP technology in previous research in the treatment of real effluents.¹¹ The combination of O_3 and H_2O_2 (O_3/H_2O_2) is denominated perozone which combines the indirect and direct oxidation of organic compounds.^{9,24} The major effects are the increase of oxidation efficiency by conversion of O_3 to HO^\bullet and the improvement of O_3 transfer from the gas to the liquid phase.²⁴ H_2O_2 will promote the

degradation of O_3 by electron transfer, or alternatively, the O_3 will activate the H_2O_2 which generates HO^\bullet and HO_2^\bullet .^{29–31}

The goal of this paper is to study the effectiveness of treatment of post oxidative effluents from a bitumen production plant with simple AOPs technology in basic pH. The novelty of this work is related with studies on effective AOPs performed exclusively at alkaline pH, due to the nature of the effluents used. Thus, the studies were performed without any pH adjustment and at their natural temperature. The studied AOPs are based on oxidation by O_3 , H_2O_2 , and peroxone. The operational parameters studied were the temperature and the ratio of oxidant in comparison with the COD of the effluents (r_{ox}). To study the efficiency of each treatment and study the degradation pathways, the chemical oxygen demand (COD), biological oxygen demand after 5 days (BOD_5), sulfide ions (S^{2-}) concentration, biotoxicity, and biodegradability were performed. In addition, this work is also focused on analysis of degradation of selected groups of VOCs, including the risk of byproducts formation.

2. EXPERIMENTAL SECTION

2.1. Materials. In these studies, real post oxidative effluents from bitumen production plant from Lotos Asphalt (Grupa Lotos, Poland) were used. The chemical characteristics of these effluents are as follows: COD between 18 and 22 g/L, BOD_5 between 4 and 6 g/L, pH of 10.5, and a S^{2-} concentration between 0.2 and 1 g/L. The temperature of these effluents at the outlet of the scrubbing system where they are generated is 40 °C hydrogen peroxide 30%, sodium sulfite nonahydrated ($Na_2S \cdot 9H_2O$) and sodium hydroxide were purchased from POCH Poland. 2% NaCl solution, lyophilized *Vibrio fischeri*, microtox diluent, microtox acute reagent, osmotic adjusting solution, and reconstitution solution were purchased from Modern Water Ltd.

2.2. Apparatus. To perform the research, an acid-resistant steel closed cylindrical reactor (Figure 1) was designed and used, with a height of 0.8 m, a radius of 0.15 m, and total volume of 15 dm³. The reactor is equipped with a Kacperek, model HM-141 Poland, stainless steel stirrer, a manometer and an APAR, model AR600, temperature regulator coupled with a 2000 W heater (Figure 1). The procedures conducted were done in semibatch mode where the oxidant was added in a continuous mode during whole time of treatment. The effluents were pumped into the reactor by a Euralca, model UGD 100/120-03, Italy membrane (PTFE) pump. Ozone was fed by a Tytan 32 ozone generator that can produce up to 70 mg O_3 /L of air. Air was used to produce ozone. H_2O_2 was fed to the reactor using a Hitachi LaChrom HPLC Pump model L-7110.

The detailed description of oxygen-VOCs (O-VOCs), volatile sulfur compounds (VSC), and volatile nitrogen compounds (VNCs) apparatus are described in our previous papers.^{36–38}

COD determination was done using a HACH COD reactor and a HACH DR/2010 spectrophotometer. The BOD_5 was determined using an Elmetron COG-1 oxygen electrode. The samples during a 5 day period of incubation were stored in an incubation chamber (Flow Laboratories catalog number S1-500-00). pH was measured by Merck nonbleeding pH paper strips. Biotoxicity results were collected using a Microtox 500 analyzer of Modern Water Ltd. Sulfide measurements were performed using an Elmetron EA/S-01 sulfide/silver electrode in combination with an Elmetron RL-100 reference electrode.

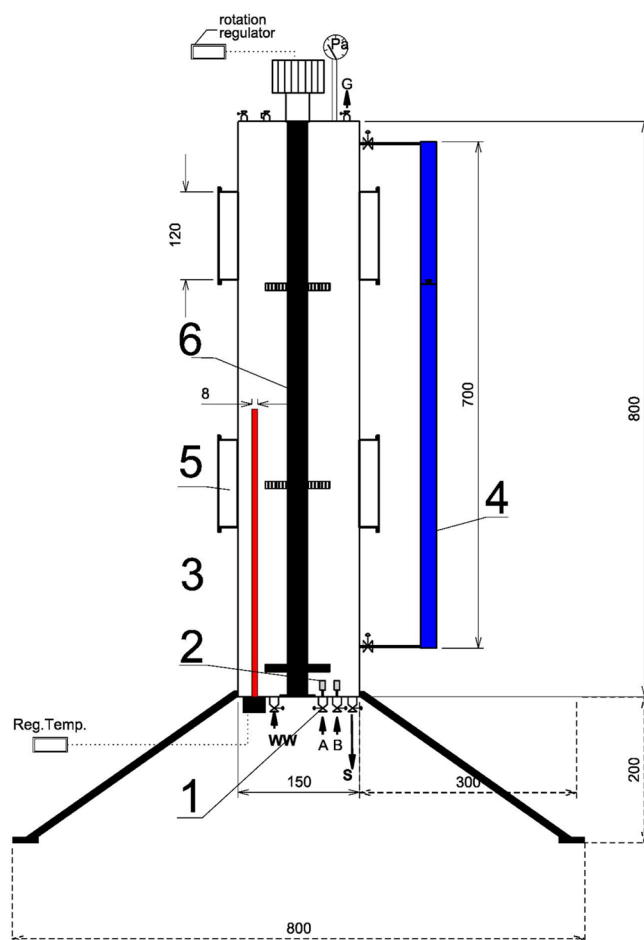


Figure 1. A scheme of the reactor designed for these studies. (1) Inlets for WW and oxidants, (2) distribution heads for oxidants, (3) heater with regulator, (4) WW level indicator, (5) window, and (6) stirrer with regulation; WW, wastewater; A,B, oxidants; S, sample collection; and G, waste gases.

The values in millivolts were read in a Elmetron CP-505 pH meter.

2.3. Procedure. **2.3.1. Effluent Treatment.** In every procedure, 5 dm³ of effluents were added to the reactor. All procedures were done at an initial pH of 10.5 and stirred at 200 rotations per minute (rpm). With regard to the H_2O_2 and ozone dose, the air flow rate and ozone concentration was established depending on the ratio between the oxidant and the COD in the effluents (r_{ox}). The calculation procedure of the amount of oxidant needed is presented in section 1. Table 1 presents the main parameters for the procedures studied. The treatment time depended on the r_{ox} . The pH was measured by pH strips in every sample taken. Regarding the ozone and peroxone procedures, due to the high amount of foam produced from the effluents, a STRUKTOL SB 2032 antifoam agent, kindly provided by ICSO Chemical Production Polska, was used in the concentration of 200 ppm (selected during preliminary studies of this project).

2.3.2. Process Control. Every sample was taken with the purpose of analyzing the VOCs concentration, COD, BOD_5 , biodegradability, biotoxicity, and sulfides concentration. All samples prior to their use in all methods studied were preserved around 5 °C. COD was measured using the Polish standard test method PN-ISO 15705:2005, based on the dichromate method by HACH. The BOD_5 was measured by the International

Table 1. Summary of the Optimal Process Parameters from Three Different Technologies^a

parameter	O ₃ /H ₂ O ₂	O ₃ /H ₂ O ₂	O ₃	O ₃	H ₂ O ₂	H ₂ O ₂
r_{ox} (w/w)	0.49	1.02	0.34	0.7	0.45	0.46
temperature (°C)	25	40	25	40	40	25
ratio (O ₃ /(H ₂ O ₂)) (w/w)	0.48	0.98	–	–	–	–
total amount of oxidant (g)	97.92	188.9	34.69	69.38	31.11	62.23
ratio of oxidant to total mass of VOCs (r_{VOCs})	154.6	298.5	102.3	109.7	49.3	188.7
time of oxidation (min)	249.6	317.1	221.1	353.9	181.5	181.5
COD degradation (%)	43	43	39	36	33	31
BOD ₅ degradation (%)	34	36	45	37	37	27
biodegradability increase (%)	16	26	–9	–2	6	–6
S ²⁻ (%)	>99	>99	>99	>99	>99	>99

^aResults of COD, BOD₅, and sulfide oxidation.

Standard Norm 5815-1, where the samples were incubated at 20 ± 1 °C.³² Biototoxicity was performed using the Microtox method using the bacteria *Vibrio fischeri*. The method is fully described in section 2.1. To determine the sulfides concentration, an ion selective electrodic system was used. The detailed method is fully described in section 2.2. With regard to VOCs monitoring, the sample preparation was done by dispersive liquid–liquid microextraction (DLLME) the analysis of obtained extracts by means of gas chromatography-mass spectrometry/flame photometric detector/nitrogen phosphorus detector (GC-MS/FPD,NPD). Details of the procedures are fully described in our previous papers.^{33–35}

2.3.3. Quality Assurance of Data. To ensure the reproducibility and the reliability of the results shown, all procedures were done in triplicate. In addition, it was supported with the analysis of COD and BOD₅ were done in triplicate for every sample, with a RSD not higher than 2%. With regard to the VOCs monitoring, the reproducibility of the methods used were evaluated and confirmed in our previous work.^{33–35}

3. RESULTS AND DISCUSSION

Post oxidative effluents from a bitumen production were submitted to treatment by three types of AOPs, O₃, H₂O₂, and O₃/H₂O₂. The parameters under study were the r_{ox} and temperature, which will be discussed in separate subsections. The parameters used for determining the efficiency of the treatments were COD, BOD₅, biodegradability, biotoxicity, S²⁻ and O-VOCs, VSCs, and VNCs controlled by GC. Table 1 summarizes the BOD₅, COD, and S²⁻ decrease after treatment. Table 2 describes the biotoxicity decrease and biodegradability increase after treatment. To make sure, that the moment of COD measurements after the treatment is not affecting the results, an additional series of experiments has been performed. COD values from the same set of samples were checked in different intervals of time after collecting the sample (48 h

Table 2. Biodegradability and Biototoxicity Results from the Optimal Processes from the Three Different AOPs

parameter	O ₃ /H ₂ O ₂	O ₃ /H ₂ O ₂	O ₃	O ₃	H ₂ O ₂	H ₂ O ₂
r_{ox} (w/w)	0.49	1.02	0.34	0.7	0.45	0.46
temperature (°C)	25	40	25	40	40	25
biodegradability increase (%)	16	26	–9	–2	6	–6
biotoxicity decrease (EC 50) (%)	54	10	138	95	–14	–57

period). The values were inside the RSD value of the COD method proving that there was no further oxidation inside the samples after their collection. These findings are supported with the fact that the amount of oxidant added continuously is very small, making it possible to be totally consumed in the aqueous matrix.

3.1. Changes in COD and BOD₅. **3.1.1. Oxidation by H₂O₂.** The analysis of results presented on Figure 1S and Table 1 revealed that in the H₂O₂ processes the COD and BOD₅ decrease was faster with the increase of oxidant dose from a r_{ox} of 0.08 to 0.45. The highest effectiveness obtained by these processes was a decrease of 33% and 37% in COD and BOD₅ values, respectively, for a r_{ox} of 0.45. However, a further increase of the r_{ox} did not result in higher effectiveness of the process. This can be related with the high amount of H₂O₂ added to the effluents which can act as a scavenger of oxidation or even dissociate in water to O₂ and H₂O.^{36,37} With a r_{ox} of 0.46 of H₂O₂ at 25 °C, a decrease of the reduction of COD was observed from 33 to 31% and a decrease of 10% on the reduction of the BOD₅ from 37 to 27%. This can be related with the high stability of the H₂O₂, which in part remains in its primary form and acts as scavenger when it is present in high amounts in the liquid phase. H₂O₂ is not thermally activated to generate HO•, and it is more stable in liquid phase at lower temperatures.^{36,37} This effect is visible for a lower r_{ox} of 0.22, where the effectiveness of the process is higher at 25 °C than at 40 °C as shown in Table 1, with an increase of the COD reduction by 11% and a decrease in BOD₅ reduction by 3%. These studies revealed that the optimal parameters for H₂O₂ processes are $r_{ox} = 0.45$ at 40 °C. The results obtained achieved higher degradation than the degradation of linear alkyl benzene wastewater (WW) with 27% of COD reduction after 180 min at pH 9.¹¹

3.1.2. Oxidation by Ozone. In the O₃ procedures, the increase of the reduction of COD and BOD₅ values was observed with the increase of the r_{ox} from 0.07 to 0.36 as demonstrated in Figure 2S. Further increasing the dose of ozone from a r_{ox} of 0.36 to 0.70 had an increase of only 6% in the COD reduction and 10% in the BOD₅. A possible explanation to this behavior can be related with the excess of ozone present which can act as a scavenger of the HO•. In addition, with the increase of the r_{ox} there is also an increase of the flow rate, decreasing the contact time of ozone and increasing the size of the bubbles inside the liquid phase. These factors affect the mass transfer and the amount of HO• decreasing it. It is interesting to observe an increase, but not significant, in the reduction of COD and BOD₅ values when the temperature decreased from 40 to 25 °C at a r_{ox} of 0.36. At a r_{ox}



of 0.7, the changes in COD were even smaller but in terms of BOD₅ there was a decrease in the reduction of these parameters. The solubility of the ozone in liquid phase is also an important parameter. It is well-known that the solubility of O₃ in the liquid is higher at lower temperatures, thus increasing the mass transfer to the liquid phase. Another important aspect is the activation energy of the oxidation reaction. Thus, the optimal parameters are a r_{ox} of 0.34 at 25 °C with 39% and 45% of COD and BOD₅ degradation, respectively. These results are similar to the other paper, which reported 37% COD reduction in the degradation of linear alkyl benzene WW.¹¹ Also winery WW achieved similar results, with 40 and 45% COD reduction at using O₃ at basic pH.^{38,39}

3.1.3. Oxidation by Peroxone. Figure 3S presents the COD reduction depending on the r_{ox} and Table 1 shows the COD and BOD₅ reduction after treatment in the peroxone processes. It is demonstrated that the COD and BOD₅ reduction increased with the increase of r_{ox} from 0.1 to 1.02. The optimal r_{ox} value was 1.02, resulting in 43% and 36% decrease of COD and BOD₅, respectively. The ratio between O₃ and H₂O₂ was 0.98 (w/w). When the r_{ox} was kept the same and the temperature was decreased to 25 °C there was an increase of the COD and BOD₅ reduction of 12% and 3% to 43% and 34%, respectively, for a r_{ox} of 0.49. The scenario changed when the r_{ox} was kept at 1.01 with a lower reduction in COD and BOD₅ values in 25 °C than in 40 °C. This is mainly due to the increase of the reaction rate constant, which allowed one to obtain higher efficiency in the analyzed time, as well as favoring the oxidation reactions which went faster, thus a larger amount of HO• radicals was used before its scavenging and conversion to less effective radicals. The optimal parameters are with a r_{ox} of 0.49 at 25 °C. Zangeneh and co-workers reported a 39% COD reduction in linear alkyl benzene using peroxone at pH 9, achieving similar effectiveness to the results reported in this work.¹¹

3.1.4. Overall Discussion. Analyzing Table 1, the effectiveness is not very high, suggesting that the effluents contains several compounds that are not degraded via oxidation using simple oxidants at basic pH. These compounds were identified in our previous work.^{1,2} The presence of aliphatic hydrocarbons can explain the low organic degradation. Furthermore, some byproducts are formed during the treatment which are not further oxidized in studied conditions. These reasons can sustain the small increase of the COD reduction when doubling the r_{ox} and the low COD degradation, making these processes suitable as a pretreatment method. This is not a disadvantage of these processes due to the fact that the typical refinery wastewater treatment plant uses an activated sludge at the biological stage of the treatment, which is able to effectively degrade the hydrocarbon pollutants. Other factors that can affect the efficiency of the process is the HO• formation and the chemistry of the studied technologies at basic pH. In the operational conditions described in this work, the H₂O₂ processes do not favor the generation of HO•. H₂O₂ at basic pH leads to the formation of perhydroxyl ions (HO₂⁻) with significantly lower oxidation power in comparison to hydroxyl radicals.²⁸ Nevertheless, it was proved that it can lower significantly the COD and oxidize effectively some groups of VOCs. This allows one to consider the H₂O₂ process as a related AOP option for effluent treatment. On the other hand, O₃ at basic pH leads to the formation of HO•,^{19,24} which can explain the higher COD reduction when comparing with H₂O₂. In the peroxone process, it is known that the dissociation of

H₂O₂ to HO₂⁻ will occur and afterward will promote more effectively the decomposition of O₃ to HO• than HO⁻.^{24,40} Therefore, the increase of effectiveness of peroxone comparing with O₃ is expected and observable in the results shown.

With regard to the BOD₅ reduction, the results are similar to the COD, with lower reduction in H₂O₂ and O₃/H₂O₂ processes comparing with COD values but with higher reduction in O₃ processes. O₃ processes were more effective in the BOD₅ reduction. BOD₅ values are related with the compounds that can be oxidized via biological processes, while the COD is related with every organic sources which can be oxidized. Results clearly show that the oxidants used can oxidize chemically and biologically degradable species with similar efficiency.

It was proved that at lower temperatures, lower amounts of oxidants are needed to reach the same effectiveness compared to 40 °C. This indicates that at higher temperature some part of the introduced oxidant decomposes without a useful effect (i.e., the oxidation reactions with organic pollutants). Nevertheless, knowing that the natural temperature of the effluents is 40 °C, additional equipment would be needed to cool the effluents to 25 °C.

3.2. Biodegradability and Biototoxicity. Biodegradability and biototoxicity were also studied for each processes described in Table 2. The biodegradability was determined by the ratio between BOD₅ and COD ($r = \text{BOD}_5/\text{COD}$). The effluent biodegradability is considered to be low with values around 0.3.⁴¹ It is interesting to see that only using peroxone processes, the biodegradability increases significantly with 16 and 26%. In the case of O₃ and H₂O₂, they had a decrease on this parameter; nevertheless, it was a decrease lower than 10%, thus this change is not really relevant. It can be stated that peroxone processes provide not only higher COD reduction but also an increase in the biodegradability, enabling the treated effluents to be more effectively degraded by microorganisms.

In addition, biototoxicity tests were performed to compare this parameter between studied AOPs. It must be highlighted that a Microtox uses a specific bacteria (i.e., *Vibrio fischeri*) which are sensitive to changes of characteristics of the effluents. Some of them are not really important in terms of WWT (i.e., lowering the pollution load and toxicity characteristics of the remaining pollutants) but strongly affect the results of measured biototoxicity. These parameters are mainly pH and salinity (i.e., the same composition of the effluents but having difference in this parameters will result in changes of the measured biototoxicity). Second, also color of the samples in some part affects the measurements. These effects are minimized by pH correction and dilution of the samples prior to analysis. Also some specific compounds formed as byproducts during treatment can be highly toxic with respect to *Vibrio fischeri*, but at the same time, they will be almost nontoxic to bacteria present in refinery activated sludge. Unfortunately, there are no available standard tests which allow one to evaluate the biototoxicity in respect to the specific bacteria present in activated sludge of particular branch of chemical industry, such as refinery WWT plants. Table 2 shows effective concentration (EC₅₀) values, which indicate the increase of the concentration of studied samples needed to obtain a decrease of chemiluminescence of 50% of population of the bacteria⁴² at the conditions described in section 2.2. This increase represents consequently the decrease of biototoxicity of the effluents treated (i.e., higher concentration of the effluents is needed to obtain the toxicity for 50% population). Looking to the results, it is



Table 3. Overall Degradation of the VOCs Using H₂O₂, O₃, and O₃/H₂O₂ Processes

compound	primary conc (mg/L)	% of compound degradation					
		H ₂ O ₂ r _{ox} = 0.46; 25 °C	H ₂ O ₂ r _{ox} = 0.45; 40 °C	O ₃ r _{ox} = 0.69; 40 °C	O ₃ r _{ox} = 0.36; 25 °C	O ₃ /H ₂ O ₂ r _{ox} = 0.49; 25 °C	O ₃ /H ₂ O ₂ r _{ox} = 1.02; 40 °C
acetaldehyde	8.05	79%	95%	82%	91%	28%	-200% ^a
1-butanol	14.61	36%	14%	65%	90%	35%	79% ^b
2-pentanone	3.33	19%	15%	>99%	98%	87%	>91%
furfural	3.08	-82% ^a	-418% ^a	99% ^b	90%	-6% ^{ab}	69% ^b
1-hexanol	4.9	36%	11%	96%	66%	76%	94% ^b
cyclohexanol	3.38	18%	-20% ^a	64%	66%	18%	66%
cyclohexanone	6.31	3%	-1% ^a	87%	57%	21%	80%
1-heptanol	1.75	34%	>94%	96%	89%	90%	>79%
phenol	16.47	>99%	93%	99%	99%	>99%	>99%
benzyl alcohol	0.85	2% ^b	5%	33%	98%	20%	>96%
acetophenone	2.49	-1% ^a	14%	>93%	69%	21% ^b	89%
o-cresol	6.27	98%	99%	>96%	97%	>96%	>96%
m-cresol	13.34	98%	98%	>98%	98%	>98%	>98%
2,6-dimethylphenol	0.72	>47%	94%	>3%	>27%	>38%	>72%
4-ethylphenol	3.22	96%	98%	>79%	>85%	>80%	>83%

^aValues show that the concentration of the compound increased after treatment. ^bValues represent an increase of the concentration of the compound in the first 60 min of oxidation and hereafter presented a stable decrease.

Table 4. Overall Degradation of the VSCs Using H₂O₂, O₃, and O₃/H₂O₂ Processes

compound	primary conc. (mg/L)	% of compound degradation					
		H ₂ O ₂ r _{ox} = 0.46; 25 °C	H ₂ O ₂ r _{ox} = 0.45; 40 °C	O ₃ r _{ox} = 0.69; 40 °C	O ₃ r _{ox} = 0.36; 25 °C	O ₃ /H ₂ O ₂ r _{ox} = 0.49; 25 °C	O ₃ /H ₂ O ₂ r _{ox} = 1.02; 40 °C
2-mercaptoethanol	2.82	>59%	>68%	>77%	>42%	>22%	>42%
thiophenol	1.22	>88%	>86%	>86%	>86%	>90%	>68%
thioanisole	0.90	>63%	>12%	>78%	>12%	>75%	>77%
dipropyl disulfide	1.34	>98%	>98%	>97%	>98%	>98%	>98%
1-decanethiol	1.20	>71%	>63%	>23%	>59%	>55%	>60%
S-X1	1.01	>99%	>99%	100%	>98%	>99%	>96%
S-X2	0.74	>98%	>98%	100%	>95%	>99%	>96%
S-X3	0.34	>98%	>97%	>98%	>96%	>98%	>84%
S-X4	0.91	>98%	>99%	>99%	>99%	>98%	>99%
S-X5	1.01	>99%	>99%	100%	>98%	>99%	>99%
sum of the S-X	4.00	>99%	>99%	>99%	>99%	>99%	>99%
sum of unidentified VSCs	2.93	48%	92%	>99%	74%	85%	>99%
total VSCs	12.54	90%	98%	>99%	94%	97%	>99%

clear that H₂O₂ processes had a decrease of the EC₅₀ value, suggesting an increase in the biotoxicity of the treated effluents. On the other hand, peroxone and O₃ processes had an increase of EC₅₀. Peroxone had an increase of 10 and 54% at 40 and 25 °C, respectively. O₃ processes increased the EC₅₀ by 95 and 138% after treatment at 40 and 25 °C, respectively. These studies revealed that lower temperatures influence positively the decrease of biotoxicity in O₃-based processes. In addition, the usage of H₂O₂ is a determinant factor for biotoxicity, increasing its value as shown in Table 2. This can be an explanation of lowering the positive effect of ozone in the case of peroxone usage. Therefore, O₃ processes were more effective to decrease the biotoxicity of the effluents, making it more favorable to be submitted to a biological stage.

3.3. Changes of Sulfides Content (S²⁻). Looking to the values after treatment, they all were under the limit of detection (LOD) which is 0.032 mg/L. Analyzing the sulfide concentration during treatment, it was proved that their oxidation occurs in the first 15 min of treatment. These results suggest that treatment using these technologies could

effectively oxidize the S²⁻ to other compounds like sulfates as described by the percentage of oxidation.⁴³ This can be useful if there is possibility to apply other types of AOP at different pH rather than alkaline. In such case, a short time of oxidation could be used to convert total sulfide ions in the effluents. After this stage, the pH could be corrected to neutral or acidic and further oxidation could use highly effective in acidic conditions AOP processes like Fenton-based technologies. The presence of sulfide ions in the effluents is an important issue, first due to its possible emission in the form of hydrogen sulfide, if the pH could be changed from basic to acidic, second due to the formation of FeS, if iron ions would be introduced into the effluent. From these reasons, it is preferred to remove sulfide ions prior to acidification of the effluents.

3.4. Volatile Organic Compounds Degradation Effectiveness. O-VOCs, VSCs, and VNCs were analyzed to evaluate in detail the course of oxidation reactions, especially the risk of harmful byproducts formation. A total number of 28 volatile organic compounds have been identified and controlled, 5 VSCs, 8 VNCs, and 15 O-VOCs. The analysis



Table 5. Overall Degradation of the VNCs Using H₂O₂, O₃, and O₃/H₂O₂ Processes

compound	primary concentration (mg/L)	% of compound degradation					
		H ₂ O ₂ $r_{ox} = 0.46$; 25 °C	H ₂ O ₂ $r_{ox} = 0.45$; 40 °C	O ₃ $r_{ox} = 0.69$; 40 °C	O ₃ $r_{ox} = 0.36$; 25 °C	O ₃ /H ₂ O ₂ $r_{ox} = 0.49$; 25 °C	O ₃ /H ₂ O ₂ $r_{ox} = 1.02$; 40 °C
1-nitropropane	1.32	77%	-1010% ^a	97%	99%	86%	>99%
pyrrole	1.07	>24%	>19%	>19%	>19%	>14%	>16%
pyrazole	5.00	>66%	>82%	>82%	15%	>71%	>32%
2,4-dimethylpyridine	0.19	>38%	-24% ^a	>16%	61%	21%	73%
2,4,6-trimethylpyridine	0.38	>67%	>85%	>87%	61%	55%	>91%
2-ethyl-1hexylamine	0.60	-459% ^a	-754% ^a	>91%	-11% ^a	53%	>93%
heptylamine	0.34	>75%	>81%	>75%	17%	>72%	38%
p-toluidine	3.53	>99%	>99%	>99%	>96%	>99%	>99%
N-X1	1.90	-980%	-3708%	>99%	92%	20%	-98%
N-X2	1.44	-2133%	-12200%	>99%	97%	39%	-215%
sum of the N-X	3.34	-1246%	-5300%	>99%	94%	29%	-143%
sum of unidentified VNCs	11.22	5%	-772,7%	85%	63%	42%	-139%
total VNCs	25.40	49%	-204,0%	87%	62%	58%	2%

^aValues show that the concentration of the compound increased after treatment.

of results presented in Table 1 reveals that the ratio of oxidant to the total mass of VOCs present (r_{VOCs}) is very high (>49), suggesting that there is enough available oxidant to degrade the VOCs with relatively high effectiveness.

Tables 3, 4, and 5 summarize the primary concentration and the percentage of degradation of the VOCs, VSCs, and VNCs after treatment in the procedures with the best performance in all three AOPs. These processes are described in Figure 2. The compounds which contain the symbol ">" had the concentration after treatment under the LOD.

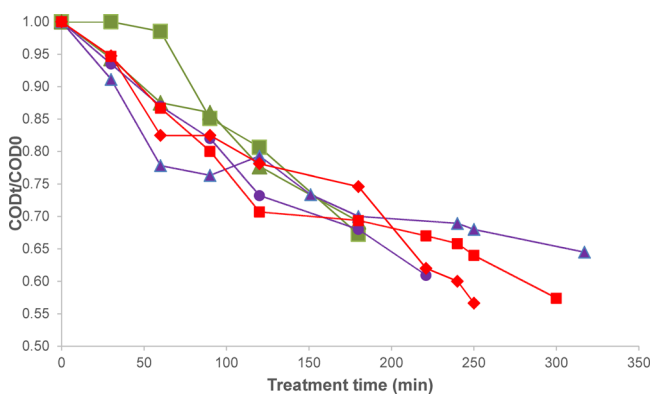


Figure 2. Profile of the COD reduction in comparison with the effect of temperature in H₂O₂, O₃, and O₃/H₂O₂ processes. Green ■, H₂O₂ $r_{ox} = 0.45$ at 40 °C; green ▲, H₂O₂ $r_{ox} = 0.46$ at 25 °C; purple ●, O₃ $r_{ox} = 0.37$ at 25 °C; purple ▲, O₃ $r_{ox} = 0.69$ at 40 °C; red ◆, O₃/H₂O₂ $r_{ox} = 0.4$ at 25 °C; and red ■, O₃/H₂O₂ $r_{ox} = 1.02$ at 40 °C.

The analysis of the results of treatment using ozone-based processes must include the phenomena of partial stripping of the volatile organic compounds from the liquid phase, as a result of vigorous gas barbotage. This effect has been evaluated in our preliminary studies for the experimental conditions described in this paper. Surprisingly, this effect was not that big as assumed. VOCs having a boiling point up to 100 °C are removed from the effluent by nitrogen (used instead of air to make sure that no oxidation by oxygen takes place, at maximal

flow rate used in this paper) barbotage at 40 °C of the effluent in less than 30% (less than 12% at 25 °C) in 360 min. The compounds with the boiling point range above 150 °C are removed in less than 10% (less than 5% at 25 °C). Analysis of the results presented in this paper relates to lowering the content of chemical compounds in the effluents prior to its WWT by biological processes. Thus, even if some part of compounds would be removed by gas stripping, they will contribute to the purpose of the process. Moreover, it is a common practice in the industry to use a thermal treatment of gases from such processes prior to its emission to atmosphere (i.e., they are used to supply flame towers, burners etc.), which convert VOCs to nontoxic carbon dioxide. That is why this effect is positive in terms of the goal of this paper.

Analyzing Table 2 regarding the aromatic compounds, O₃ with a r_{ox} of 0.34 at 25 °C is the most effective and optimal process. Benzyl alcohol and acetophenone were compounds more persistent to degradation in all three technologies studied, especially in the H₂O₂ processes, proving that the sole use of H₂O₂ is not providing an effective degradation. Aromatics presented a slow degradation rate in the first 30 to 60 min, but hereafter, the rate increases significantly. Some processes only start to have an increase of the reaction rate after 60 min. These results are supported by Table 1S. On the other hand, the effluents treated with sonocavitation revealed an increase of this compound after treatment.³³

Analyzing the ketone and alcohol compounds group, O₃ and peroxide processes at 40 °C revealed to be more effective degrading these compounds. In respect to the H₂O₂ processes, they revealed to be persistent to degradation, achieving degradation under 36% after treatment with the exception of 1-heptanol. A possible reason for such behavior is the higher oxidation potential of O₃ and its capability of producing more reactive radicals and the incapability of H₂O₂ solely to degrade these compounds. In addition, in the O₃ and peroxide processes, the temperature played an important role. At 25 °C, the efficiency of degradation was very low, which is related with energy of activation. Thus, for these compounds, an increase of temperature and r_{ox} is needed to achieve high degradation effectiveness. The results of degradation are similar

for 1-heptanol, 2-pentanone, and higher for cyclohexanone, when comparing with the same type of effluents treated with sonocavitation.³³ Comparing O_3 and O_3/H_2O_2 , it can be concluded that O_3 is the best technology to degrade ketone compounds.

In addition, the increase of concentration of other compounds in the first 60 min like 1-butanol, 1-hexanol, and the aldehyde-furfural was also reported. This clearly shows that during the first 60 min of oxidation, these compounds are byproducts of oxidation of other compounds. After the first 60 min, the byproduct formation inhibits (probably due to the total degradation of compounds responsible to form these compounds), and the degradation takes place until the end of treatment.

With regard to the VSCs, they achieved high degradation efficiencies, with values after treatment below LOD in all studied procedures. Table 3 presents the degradation of each VSCs after treatment. In addition, a quantification for 5 unidentified peaks having the highest concentration was performed using the procedure described in our previous work.³⁴ These unidentified compounds (S-X1 to S-X5) also were effectively degraded to a concentration level under the LOD after treatment, reaching more than 99% of degradation in the majority of the processes. Analyzing Table 2S, the degradation rate was high, reaching values lower than the LOD in less than 30 min for almost all O_3 processes, in less than 60 min for O_3/H_2O_2 and H_2O_2 processes. All technologies achieved effective total VSCs degradation with more than 90% degradation in all processes. O_3/H_2O_2 processes at a r_{ox} of 1.02 at 40 °C had the highest efficiency with a total VSCs degradation higher than 99%. These findings can be supported by our previous works.^{1,2}

Table 4 compares the degradation of the VNCs in the three different AOPs exhibiting different behaviors. Two unidentified peaks, N-X1 and N-X2, were quantified using the same approach described in our previous work.³⁵ 2-Ethyl-1-hexylamine revealed to be a byproduct of oxidation of other compounds in H_2O_2 processes with a significant increase of concentration. In addition, it revealed to be persistent to degradation at 25 °C in O_3 and O_3/H_2O_2 processes. The same behavior occurred with the aldehyde furfural. O_3 with a r_{ox} of 0.69 at 40 °C was the most effective process to remove VNCs, with 87% degradation of the total VNCs. It is proved that temperature influences the effectiveness of degradation. A possible explanation is already described above in the ketone compound discussion.

With regard to the the unidentified peaks, they had a significant increase after treatment in the H_2O_2 processes regardless of the temperature or r_{ox} . It was proven that these peaks are present in low concentration in primary effluent and mainly are byproducts from oxidation of the higher molecular compounds containing nitrogen. In the O_3 process, the scenario was different with a decrease higher than 94% after treatment in both peaks. In O_3/H_2O_2 , the temperature influence of N-X1 and N-X2 degradation was strongly visible, where at 25 °C there was a decrease while at 40 °C an increase of the area of the peaks was reported. This clearly shows that at 25 °C these compounds are degraded and they are not formed as byproducts. At higher temperature, the activation energy of oxidation of high-molecular compounds is lowered, which results in its degradation and formation of byproducts in the form of compounds N-X1 and N-X2. Looking to the total

VNCs concentration, O_3 processes were more effective to degrade VNCs.

With regard to the overall degradation of the VOCs, O_3 processes were more effective, especially at 25 °C with a r_{ox} of 0.34. As mentioned above, at this temperature the effect of gas stripping of VOCs from the reactor has a small influence on the measured final concentrations in the effluent. In addition, the ratio of oxidant to the total amount of VOCs (r_{VOCs}) is not directly related with the efficiency of the VOCs degradation. The r_{VOCs} in O_3 processes were lower than peroxone and one H_2O_2 processes as described in Table 1 and reached higher efficiency on VOCs degradation. Our research proved that, along with effective degradation of total load of pollutants, the studied AOPs allowed one to decrease the total content of volatile organic compounds. This phenomenon has an important practical value due to the lowering of malodorousness of the effluents. The emission of these compounds is eliminated in a single-step process and at the same time nonbiodegradable, and persistent compounds are degraded to simpler compounds, which makes the use of biological methods easier. It is a commonly used practice to perform the biological stage of treatment at open-air reservoirs, which can cause an emission of VOCs to the atmosphere. Substantial decrease of content of VOCs along with decrease of total load of pollutants proves that studied processes have applicational value for real wastewater treatment plants. In addition, it was proved that some compounds are byproducts of oxidation of others present in the effluents, namely furfural, 1-hexanol, and 2-ethyl-1-hexamine, due to their increase of concentration during treatment.

3.5. Economical Evaluation. The detailed description of the methodology used in this part is described in section 3, which followed the same methodology used in our previous work¹³ and by Mahamuni and Melin.^{44,45} Table 4S presents the main values from the economical evaluation performed. The best process of each technology studied in removing COD was only taken into account. It is observable that the cheapest technology was in fact H_2O_2 , in the total cost per year, per batch and price of chemicals and energy per batch with 114.71 thousand American Dollars (k\$), 72 \$, and 42.5 \$, respectively. In addition, it was also the processes that can treat higher volume of wastewater 15930 m³ calculated as a number of batches per year. Peroxone technology revealed to be more expensive to treat the postoxidative effluents, with a cost per year, batch, and total cost of chemicals and energy of 164.5 k\$, 402.3 k\$, and 364.4 k\$, respectively. O_3 revealed to be able to treat the less amount of effluents per year, 12140 m³. It is observable that the simpler the technology, the cheaper the treatment cost due to the similarity of the time of treatment and reaction rate constant.

Analyzing Table 4S, the total cost of the treatment depends essentially from the operational and maintenance (O and M). In addition, the cost of chemicals and energy plays a crucial role in the O and M costs, especially in the processes which used ozone, representing 71% of the cost per batch for O_3 and 90% for the peroxone process. Overall, the treatment costs of O_3 and O_3/H_2O_2 are expensive, especially if used as a pretreatment method. H_2O_2 revealed to have more realistic values. These results are similar to the generality of economical evaluation performed in real WW using this type of AOP.¹³

4. CONCLUSIONS

The research on selection of optimal conditions for effective degradation of postoxidative effluents from bitumen production were done using simple AOPs, namely, O_3 , O_3/H_2O_2 , and H_2O_2 . The optimal parameters for organic degradation for O_3 were a r_{ox} of 0.34 at 25 °C, for O_3/H_2O_2 a r_{ox} of 0.49 at 25 °C, and for H_2O_2 a r_{ox} of 0.45 at 40 °C. These studies surprisingly revealed that in the case of basic pH and treatment of such a specific effluents, lower temperature allowed one to obtain better results in terms of total degradation. The most effective AOP was O_3/H_2O_2 at a r_{ox} of 0.49 at 25 °C, with 43 and 34% COD and BOD_5 reduction. O_3 at r_{ox} of 0.34 at 25 °C was the most effective process to decrease the biotoxicity of the treated effluents. Sulfide ions (S^{2-}) were effectively oxidized in all procedures. This is important if there is opportunity to use other types of AOPs at a lower pH, like Fenton. VSCs were effectively degraded in all technologies. VNCs were a group of compounds the most persistent to degradation from all VOCs studied. O_3 at a r_{ox} of 0.34 at 25 °C was the most effective to degrade the overall VOCs. The H_2O_2 process was more problematic to degrade VOCs. Compounds like furfural and 2-ethyl-1-hexylamine revealed to be by-products of oxidation of other compounds. This phenomenon participated in the effect of increased biotoxicity of H_2O_2 processes. The economical evaluation revealed that the H_2O_2 process was the cheapest technology studied with a total cost per batch 72 \$ and peroxone the most expensive with a total cost per batch 402.3 \$. The treatment costs of O_3 and O_3/H_2O_2 technologies were expensive and not feasible. It was proved that detailed process control is a must due to the formation of byproducts. In certain cases, the formed byproducts can be highly toxic to the activated sludge of the biological treatment plant. This aspect must be analyzed during selection of the optimal method of chemical WW treatment. In addition, good effectiveness in the degradation of the volatile organic compounds and the decrease in the biotoxicity in O_3 related processes are other important outcomes of this research.

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■ ABBREVIATIONS

AOPs = advanced oxidation processes; BOD_5 = biological oxygen demand at 5 days; CO_2 = carbon dioxide; COD = chemical oxygen demand; DLLME = dispersive liquid–liquid micro extraction; EC_{50} = concentration of sample needed to reduce 50% of the bioluminescence of the bacteria; GC-MS/FPD/NPD = gas chromatography–mass spectrometry/flame photometric detector/nitrogen phosphorus detector; HO^\bullet = hydroxyl radicals; H_2O = water; H_2O_2 = hydrogen peroxide; HO_2^- = perhydroxyl ions; k\$ = thousand American dollars; LOD = limit of detection; O and M = operational and maintenance; O-VOCs = oxygen volatile organic compounds; O_3 = ozone; O_3/H_2O_2 = peroxone; r_{ox} = the ratio between the oxidant in comparison with the COD of the effluents; S^{2-} = sulfide ions; VOCs = volatile organic compounds; VNCs = volatile nitrogen compounds; VSCs = volatile sulfur compounds; WW = wastewater

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