Study of different Advanced Oxidation Processes for wastewater treatment from petroleum bitumen production at basic pH
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1. Calculation of the amount of oxidant needed depending on the ratio of oxidant in comparison with the COD of the effluents (r_{ox}) (w/w).

Oxygen present in the effluents

$$O2_{COD} = COD \ X \ V$$

Where V is the volume of water treated in L. Thus the amount of oxygen from the radicals

$$O2_{ox} = O2_{COD} \times r_{ox}$$

The $O2_{ox}$ is the same amount needed from the oxidant to give the following r_{ox} for the H_2O_2 and O_3 processes. For O_3/H_2O_2 $O2_{ox}$ is converted to mols and divided by 0.667 due to the stoichiometry of the reaction of formation of radicals. Afterwards the mols are converted to grams in order to determine the amount of oxidant needed for the Peroxone process.

2. Materials and Methods

2.1. Microtox method for determination of biotoxicity

To perform the biotoxicity tests, it was used the method from Microtox ® using the bacteria *Vibrio fischeri*. The first step involved the bacterial suspension preparation, by dissolving lyophilized bacteria in 1 ml of reconstitution solution at 5 °C. Afterwards, bacterial suspension was diluted in a proportion of 1:10 in a different vial to prepare a diluted bacterial suspension. A series of sample dilutions were prepared. It was prepared with 4 dilutions in serie starting from a vial containing, 1900 µl of diluent solution, 100

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µl of sample (dilution 1:20) and 200 µl of osmotic adjusting solution. The dilutions in serie were made with 1 ml of diluents solution and 1 ml of the previous dilution. Afterwards 2 control samples were prepared adding 1 ml of diluent solution. Afterwards 100 µl of the diluted bacterial suspension were added to new vials in a equal number of diluted samples plus the control samples. Afterwards it was read the initial bioluminescence of the diluted bacteria suspension. Next, it was transferred 1 ml of the diluted samples and control samples to the diluted bacterial suspension vials and the incubation started at 15 °C during 30 min. After incubation it was read the final bioluminescence of the samples with the diluted bacterial suspension and EC_{50} values were obtained.

2.2. Sulfide concentration determination by electrodic method

A proper calibration curve was done previously with known standard solutions of $Na_2S.9H_2O$. After the preparation of each standard, alkalization was performed by adding 0.01 dm^3 of 10M NaOH per each 0.1 dm^3 of standard. Afterwards 10ml of each sample were added to 0.1 dm^3 of 1M KNO_3. Resulting solution was stirred and both electrodes were immersed where the resulting mV were recalculated to $[S^{2-}]$ according to the calibration curve.

3. **Economical evaluation**

A detailed economic cost evaluation of each studied AOP technology was performed using the methodology used in Mahamuni and Melin [44,45]. The following assumptions were made. The evaluation was made considering that the technologies studied will be used as a pre-treatment method. The treatment plant will work 365 days per year in a semi-batch mode, where each batch will treat 10 m^3. The time of treatment was determined using the reaction rate constant (k) determined according to the

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standard procedures. With the k value it was determined the time of treatment to assure 50% COD removal. Knowing the time of treatment of 10 m^3 it was possible to know the number of batches performed in 1 year and the volume treated per year. To estimate the price of the reactor it was followed the methodology of obtaining direct quotations of companies producing the reactor and main equipment like ozone generator and pump. A quotation from a consultation company, Enertagus, indicated a price for a mixing tank of 11 130 American Dollars ($) with 10 m^3 capacity. A Tytan 32 from EREM, Poland, capable of producing 32 g/h of O_3 was chosen as an ozone generator. The quotation received indicates a price of 7600 $. Regarding the H_2O_2 processes a membrane PTFE pump was selected to pump the oxidants to the reactor. The cost of the 2 kW pump is quoted in 2000 $. Capital and amortization costs were determined by the same methodology explained by Mahamuni and Melin [44,45]. The total capital cost is the sum of the pipes, site work, contractor, engineering and contingency costs. To determine the amortization costs it was assumed that the investment was amortized in 20 years with an amortization rate of 5%. The total operation and maintenance (O&M) costs were determined as the sum of the replacement, labor, chemical and energy costs. Chemical costs were obtained from the industrial market having H_2O_2 a price of 500 $/ton. The antifoam agent price was obtained by a quotation from the same company that provided the chemical. It has a price of 3.77 $/kg. The price of energy obtained from Energa, S.A. Poland, is defined as 0.1015 $/kWh, valid for industry clients. The labor costs were determined in order to have three specialized workers during a day. The total cost of a specialized person working in such facility in Poland is around 800 $. These workers are responsible for analytical procedures, to check the performance of the process, maintenance of equipment, to ensure the hygiene and safety standards and good working conditions in the plant. The total cost per year is the sum of O&M and

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amortization costs. The total cost per batch is determined dividing the total cost per year by number of batches. In addition the total cost of chemicals and energy per batch is determined by dividing the total chemical and energy costs per year by the number of batches.

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Figure 1S. COD reduction in comparison with oxidation time for different r_{ox} values in the H_2O_2 processes.

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Figure 2S. COD reduction in comparison with oxidation time for different r_{ox} values in the O_3 processes.

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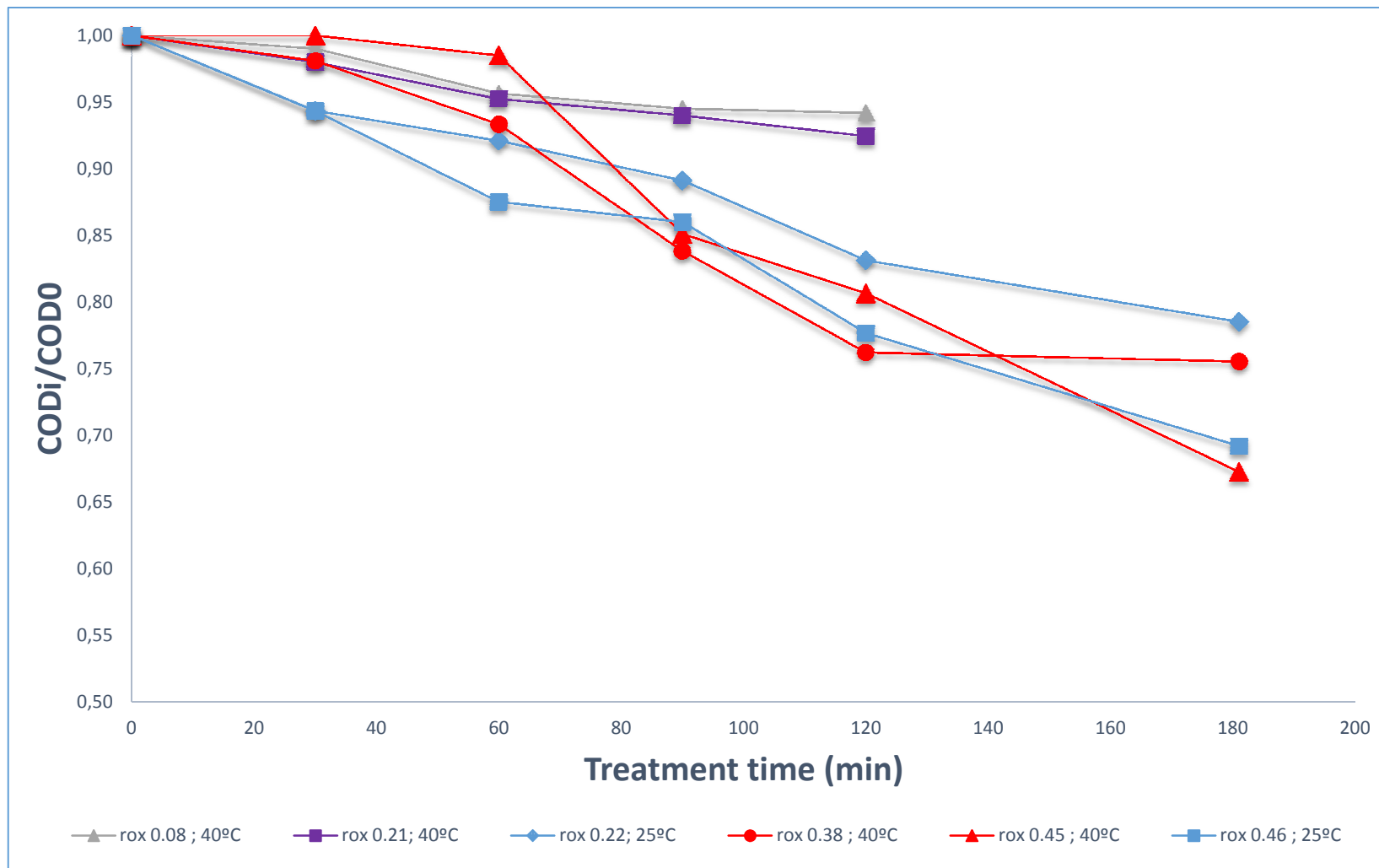
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Figure 3S. COD reduction in comparison with oxidation time for different r_{ox} values in the O_3/H_2O_2 processes.

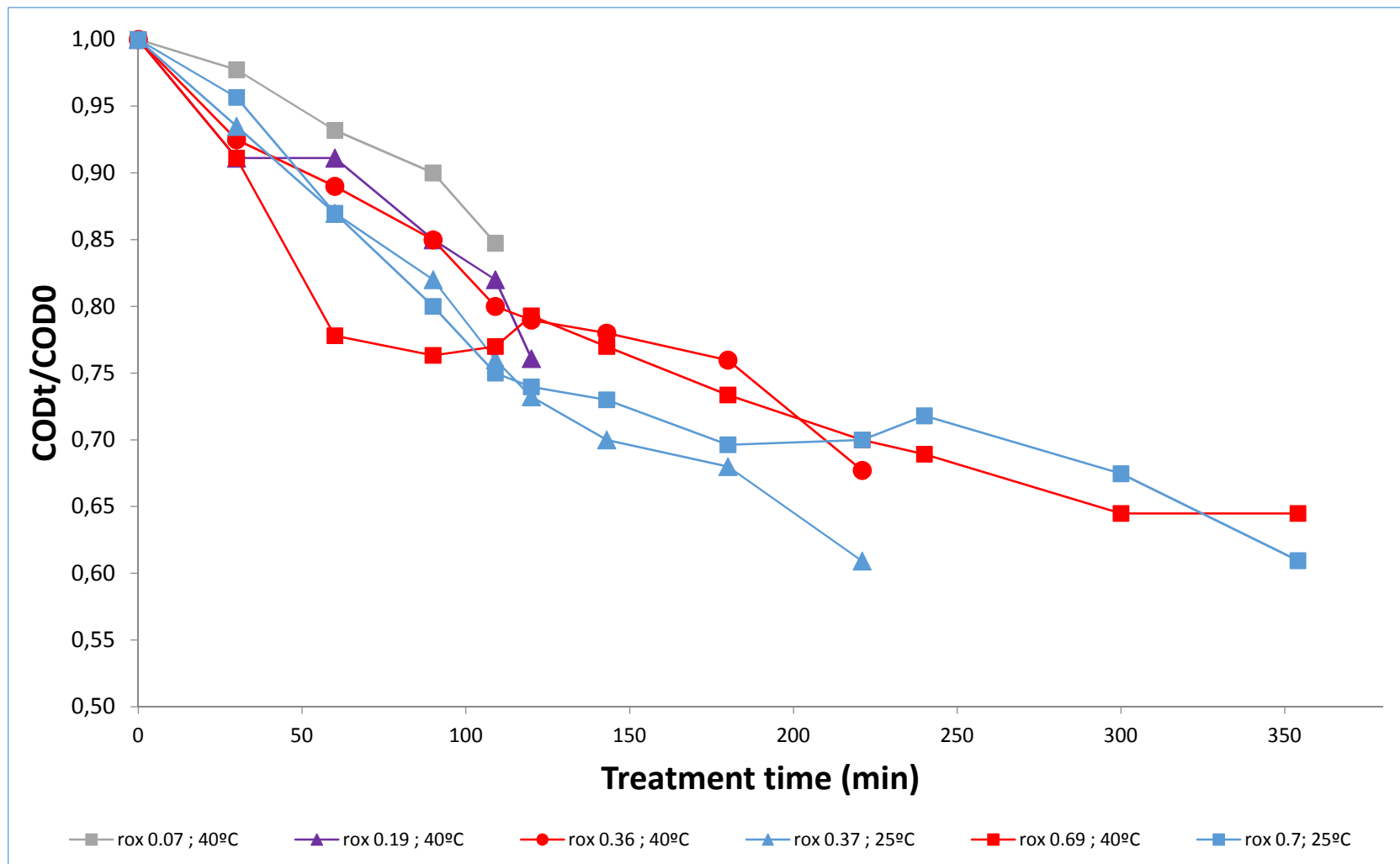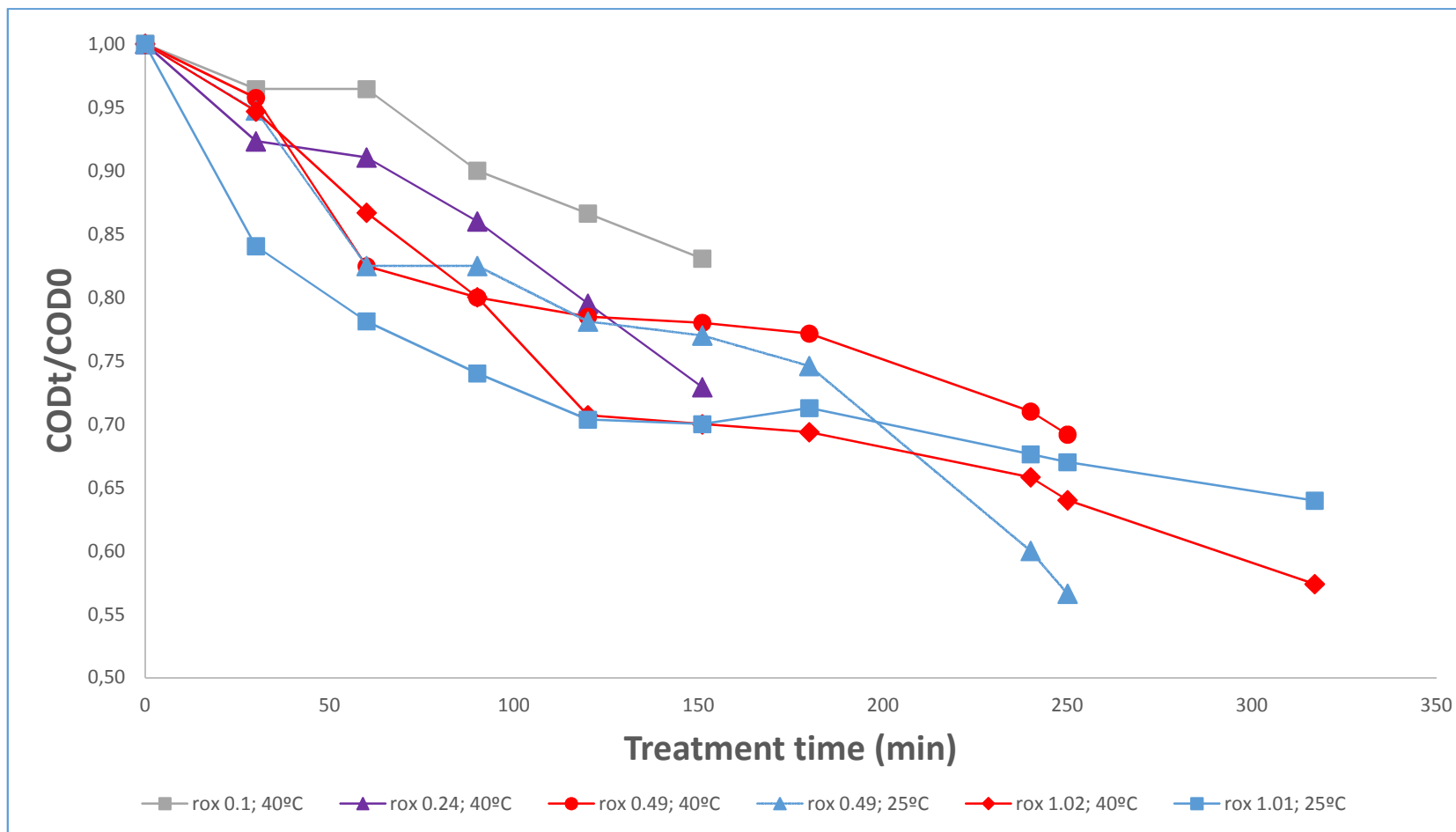G. Boczkaj, A. Fernandes, P. Makoś, Study of different Advanced Oxidation Processes for wastewater treatment from petroleum bitumen production at basic pH,

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Table 1S. Degradation of VSCs and O-VOCs during treatment time in the H_2O_2 processes

	H_2O_2 r_{ox} 0.45; 25 ºC						H_2O_2 r_{ox} 0.46; 40 ºC					
	Concentration [ppm]						Concentration [ppm]					
oxidation time (min)	0	15	30	60	120	180	0	15	30	60	120	180
2-mercaptoethanol	2,82	-	-	-	-	-	3,64	2,59	-	-	-	-
Thiophenol	1,47	-	-	-	-	-	1,22	-	-	-	-	-
Thioanisole	0,81	0,67	-	-	-	-	0,34	0,23	-	-	-	-
Dipropyl disulfide	1,34	-	-	-	-	-	1,34	-	-	-	-	-
1-decanethiol	1,70	0,15	0,06	-	-	-	1,34	0,97	-	-	-	-
acetaldehyde	15,08	5,62	5,67	0,85	1,41	3,1	10,84	6,94	2,3	-	-	0,54
1-butanol	40,59	36,26	36,89	33,82	28,02	26,17	8,51	8,46	8,68	8,42	8,37	7,31
2-pentanone	3.34	2.86	2.80	2.69	2.68	2.71	3,29	3,29	3,18	3,12	2,98	2,81
furfural	1,29	3,69	5,85	3,36	3,21	2,35	2,15	3,47	7,72	8,13	9,03	11,13
1-hexanol	5,11	11,32	11,22	11,34	11,36	3,28	5,24	5,3	5,36	5,48	5,5	4,65
cyclohexanol	3,97	5,7	5,62	5,66	5,41	3,24	3,25	3,52	3,79	3,82	3,84	3,91
cyclohexanone	9,94	9,78	9,69	9,7	9,66	9,69	2,01	2,11	2,09	2,08	2,06	2,04
1-heptanol	1,54	1,49	1,2	1,04	1,03	1,01	4,38	3,96	3,49	3,31	3,22	-
phenol	16,28	19,99	16,29	13,7	7,73	-	29,21	28,97	28,34	28,03	28,32	2,15
benzyl alcohol	1,28	1,28	1,3	1,32	1,3	1,25	0,43	0,44	0,43	0,42	0,43	0,41
acetophenone	2,89	2,93	2,9	2,86	2,98	2,92	3,66	3,44	3,37	3,12	3,17	3,13
o-cresol	7,89	6,95	6,21	4,9	1,57	0,15	9,83	9,84	8,81	7,61	7,82	0,13
m-cresol	17,16	15,7	13,57	11,5	4,4	0,29	18,73	18,38	16,43	15,24	15,26	0,46
2.6-dimethylphenol	0,66	0,44	0,59	0,31	-	-	1,04	0,94	0,86	0,45	0,49	0,06
4-ethylphenol	3,95	3,72	3,41	2,71	1,14	0,17	4,4	4,2	4,08	3,07	4	0,1

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Table 2S. Degradation of VSCs and O-VOCs during treatment time in the O_3 processes

	O_3 r_{ox} 0.36; 25 °C						O_3 r_{ox} 0.69; 40 °C						
	Concentration [ppm]						Concentration [ppm]						
oxidation time (min)	0	15	30	60	120	220	0	15	30	60	120	240	350
2-mercaptoethanol	1,99	1,51	-	-	-	-	5,05	0,65	-	-	-	-	-
Thiophenol	1,22	-	-	-	-	-	1,22	-	-	-	-	-	-
Thioanisole	0,34	0,17	-	-	-	-	1,34	-	-	-	-	-	-
Dipropyl disulfide	1,34	-	-	-	-	-	1,13	0,51	-	-	-	-	-
1-decanethiol	1,2	-	-	-	-	-	0,64	0,15	-	-	-	-	-
acetaldehyde	15,08	3,39	-	1,42	1,45	1,39	3,92	2,43	1,48	1,3	1,84	1,22	0,72
1-butanol	33,97	31,19	16,57	13,39	4,14	3,42	2,1	1,32	1,14	0,85	0,72	0,64	0,73
2-pentanone	3.18	2.52	2.31	2.06	0.53	0.05	3.21	1.17	0.52	0.27	-	-	-
furfural	7,09	6,08	1,26	1,34	1,45	0,69	5,63	7,97	3,54	3,42	2,74	0,97	0,08
1-hexanol	4,53	3,27	3,3	3,31	2,35	1,54	5,47	3,87	3,83	1,56	0,99	0,4	0,2
cyclohexanol	3,73	1,95	1,9	1,83	1,29	1,28	2,44	1,98	2,01	1,82	1,48	1,38	0,87
cyclohexanone	7,18	3,56	3,5	3,69	3,6	3,11	5,54	4,47	4,21	3,22	2,55	1,4	0,7
1-heptanol	1,52	0,7	0,55	0,49	0,33	0,16	0,81	0,58	0,52	0,26	0,15	0,12	0,03
phenol	14,29	7,08	5,27	5,13	1,34	0,1	11,87	9,15	7,61	4,69	0,11	0,04	0,08
benzyl alcohol	1,3	0,29	0,22	0,23	0,12	0,03	0,64	0,54	0,6	0,51	0,55	0,38	0,43
acetophenone	2,71	1,35	1,16	1,17	1,07	0,85	1,88	1,43	1,29	0,94	0,65	0,3	-
o-cresol	5,32	2,65	1,92	1,76	0,5	0,14	4,27	3,15	2,53	1,31	-	-	-
m-cresol	11,69	5,6	4,36	3,61	0,91	0,27	9,22	6,76	5,24	2,54	-	-	-
2.6-dimethylphenol	0,48	0,25	0,1	0,03	-	-	0,36	0,17	0,1	-	-	-	-
4-ethylphenol	3,37	1,57	1,1	0,76	0,22	-	2,28	1,5	1,07	0,49	-	-	-

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Table 3S. Degradation of VSCs and O-VOCs during treatment time in the O_3/H_2O_2 processes

	O_3/H_2O_2 r_{ox} 0.49; 25 ℃						O_3/H_2O_2 r_{ox} 1.02; 40 ℃						
	Concentration [ppm]						Concentration [ppm]						
oxidation time (min)	0	15	30	60	120	250	0	15	30	60	120	240	317
2-mercaptoethanol	1,47	0,47	-	-	-	-	1,97	0,65	-	-	-	-	-
Thiophenol	1,67	1,34	-	-	-	-	0,53	-	-	-	-	-	-
Thioanisole	1,22	0,6	0,19	0,19	-	-	1,32	1,24	0,45	-	-	-	-
Dipropyl disulfide	1,39	1,14	0,55	0,46	-	-	1,51	-	-	-	-	-	-
1-decanethiol	1,08	1,24	0,14	0,15	-	-	1,24	0,99	0,46	-	-	-	-
acetaldehyde	3,25	2,84	2,68	2,33	2,39	2,48	0,13	0,62	0,58	0,88	1,04	2,7	0,39
1-butanol	1,03	0,84	0,73	0,84	0,72	0,67	1,45	6,16	4,77	3,85	2,37	1,1	0,3
2-pentanone	3.63	2.94	1.51	1.52	0.68	0.51	3.31	1.62	0.61	-	-	-	-
furfural	1,44	1,81	2,2	3,12	2,93	1,53	0,89	2,06	2,65	3,01	2,41	0,65	0,28
1-hexanol	5,21	5,21	2,7	2,7	2,71	1,24	3,85	5,45	4,22	2,78	0,49	0,27	0,22
cyclohexanol	3,75	3,72	3,65	3,71	3,28	3,06	3,11	2,83	2,71	2,35	2,09	1,28	1,05
cyclohexanone	6,95	6,75	6,7	7,49	6,21	5,46	6,25	5,97	5,46	4,23	3,58	2,1	1,23
1-heptanol	1,07	1,07	0,9	0,13	0,09	0,11	1,17	0,48	0,55	0,24	0,07	-	-
phenol	13,96	13,43	12,15	11,24	0,2	-	13,2	12,18	9,7	0,46	-	-	-
benzyl alcohol	0,76	0,73	0,72	0,8	0,7	0,61	0,67	0.65	0.59	0.51	0.43	0.3	-
acetophenone	1,87	1,94	2,19	2,29	1,85	1,47	1,93	1,64	1,46	1,07	0,82	0,43	0,21
o-cresol	5,24	4,9	4,25	3,75	-	-	5,06	4,4	3,63	0,25	0,06	-	-
m-cresol	11,74	10,96	8,95	7,62	0,27	-	11,5	9,45	7,42	0,51	-	-	-
2.6-dimethylphenol	0,56	0,44	0,31	0,18	-	-	1,24	0,42	0,18	-	-	-	-
4-ethylphenol	2,51	2,44	1,91	1,56	-	-	2,83	2,03	1,51	0,21	0,07	-	-

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Table 4S. summary of the treatment costs for each technology. t 50 represents the treatment time needed to achieve 50% of COD removal. O&M means operational & maintenance. Prices in American dollars ($).

Technology	k (min^{-1})	t_{50} (h)	Price of AOP reactor (k$)	Total capital costs (k$)	Amortization costs (k$)	Total O&M costs (k$)	Total cost /year(k$)	Volume treated /year (m^3)	Cost of chemicals and energy/batch ($)	Total cost/batch ($)
H$_2$O$_2$	2.10E-03	5.50	13.13	29.17	2.81	111.91	114.71	15930	42.48	72.01
O$_3$	1.60E-03	7.22	18.73	41.61	4.01	164.48	168.48	12140	98.89	138.78
O$_3$/H$_2$O$_2$	1.70E-03	6.80	20.73	46.06	4.43	514.58	519.02	12900	364.41	402.34