

OXIDATION OF ORGANIC COMPOUNDS IN WASTE WATER WITH OZONE AND HYDROGEN PEROXIDE

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Abstract. The waste water of the wood barking department of the Enso-Gutzeit OY Varkaus factory was studied. High pressure liquid chromatography (Hewlett Packard 1050) was used to analyse the waste water. The influence of ozone and hydrogen peroxide on the organic compounds in waste water was studied. The changes in the UV absorbance at 254 nm, COD, and BOD were observed. Simultaneous application of ozone and hydrogen peroxide was found to be more efficient than simple ozonation.

Key words: waste water, ozone, hydrogen peroxide, COD, BOD, high pressure liquid chromatography.

INTRODUCTION

The composition and characteristics of waste waters of different origin vary. The pulp and paper industry is one of the industries generating large amounts of waste water [1]. The worldwide yearly output of cellulose is over 160 million tons. In the cellulose industry the wood is usually barked by the damp method. The wood barking department produces about 5% of all waste water in a cellulose factory.

The treatment of the waste water with ozone and hydrogen peroxide was studied. In [2] the elimination of atrazine in the Seine River water was studied. Results showed better degradation of atrazine in the water treated with a combination of ozone and hydrogen peroxide than ozone alone. Results of the action of ozone and hydrogen peroxide on oxalic acid were presented in [3]. The radical-producing system was much more effective at pH values appropriate to natural water. In [4] UV absorbance at 254 nm was studied. The changes in UV absorbance at 254 nm were observed in a lake water. The absorbance of water was efficiently reduced in the ozone and hydrogen peroxide system. The ozone and hydrogen peroxide system has also been studied for the oxidation of organic substrates that may be found in different waste waters [5–7].

EXPERIMENTAL

Waste waters of a wood barking department were used in this study. The samples were taken from the Enso-Gutzeit OY Varkaus factory.

The chemical composition of waste water was analysed on a Hewlett Packard 1050 series high pressure liquid chromatograph (HPLC) with an HP 1040M series II diode-array detector. The column was HP LiChrosper 100 RP-18, 5 μm , 125 \times 4 mm. The mobile phase was 0.005 M phosphate buffer and acetonitrile content varied from 30 to 70% (from 6 to 20 min). The flow rate was 1 ml/min. Ozone and ozone hydrogen peroxide experiments were conducted in a batch mode in a bubble column with a volume of 3400 ml, height 60 cm, and diameter 9 cm. The hydrogen peroxide concentration was 0, 1, 3, and 10 mM. Ozone was generated from air by a laboratory scale ozone generator Sandler Ozonizer Model 200.

The gas-phase ozone concentration at the inlet and outlet of the reactor was monitored titrimetrically with potassium iodide solution using the International Ozone Association Standard Method 001/87 and the measurement of residual ozone in water was performed by the IOA Standard Method 004/89.

RESULTS AND DISCUSSION

The chemical composition of the waste water was studied by HPLC. The chromatogram of waste water is shown in Fig. 1. The highest peak could be methylphenol.

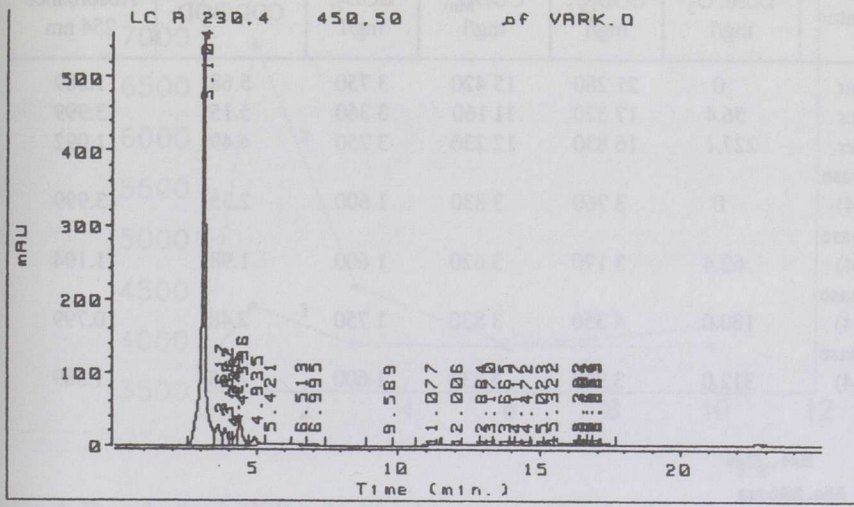
The waste water from the Varkaus factory was ozonated in the following ways:

- a) the original waste water;
- b) waste water diluted with distilled water (1:4);
- c) the above-mentioned diluted waste water with hydrogen peroxide.

The ozone dosages were approximately 2.0 mg/min.

The main results of the ozonation of the waste water from the Varkaus factory are presented in the Table. The results show that the COD, BOD, and UV absorbance values are unstable and change depending on the ozone quantity. The best upshot was achieved by adding hydrogen peroxide.

The ozone/hydrogen peroxide system has greater influence on the UV absorbance at 254 nm of the waste water by the hydrogen peroxide concentrations of 1 mM and 3 mM (Fig. 2). The further addition of hydrogen peroxide and ozonation did not give better results. The absorbance at a wavelength 254 nm indicated the presence of conjugated double bonds. The absorbance of waste water was reduced from 100% to 15% with hydrogen peroxide concentration from 0 mM to 6 mM, respectively.



LC A 230,4 450,50 of VARK.D
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Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	3.104	BV	0.120	4959	2.502	3.489
2	3.617	VV	0.173	326.44	3.489	3.749
3	3.862	VV	0.148	234.56	3.749	4.010
4	4.078	VV	0.099	51.53	4.010	4.126
5	4.245	VV	0.105	93.11	4.126	4.273
6	4.396	VV	0.155	399.46	4.273	4.724
7	4.935	VV	0.201	147.27	4.724	5.304
8	5.421	VV	0.197	20.92	5.304	5.954
9	6.513	BV	0.150	5.20	6.246	6.776
10	6.995	VV	0.192	20.73	6.776	7.429
11	9.589	BV	0.194	3.35	8.859	9.830
12	11.077	PV	0.271	8.37	10.619	11.436
13	12.006	VV	0.246	10.22	11.513	12.241
14	12.884	VV	0.263	7.07	12.241	12.899
15	13.170	VV	0.257	9.47	12.899	13.339
16	13.665	VV	0.258	19.89	13.339	13.958
17	14.117	VV	0.125	3.74	13.958	14.140
18	14.472	VV	0.297	11.56	14.140	14.646
19	15.023	VV	0.249	17.53	14.646	15.139
20	15.322	VV	0.218	19.61	15.139	15.480
21	16.322	VV	0.421	75.38	15.480	16.367
22	16.404	VV	0.057	9.41	16.367	16.444
23	16.622	VV	0.141	24.67	16.444	16.646
24	16.823	VV	0.147	24.87	16.646	16.850
25	16.883	VV	0.271	46.43	16.850	17.680

Fig. 1. HPLC chromatogram of diluted waste water.

Waste water parameters

Waste water	Dose, O ₃ mg/l	COD _{Cr} , mg/l	COD _{Mn} , mg/l	BOD ₇ , mg/l	COD/BOD	Absorbance 254 nm
Base water	0	21 280	15 420	3 750	5.68	1.589
Base water	56.4	17 320	11 160	3 360	5.15	3.999
Base water	227.1	16 830	12 230	3 750	4.49	1.092
Diluted base water (1:4)	0	3 760	3 830	1 600	2.35	3.999
Diluted base water (1:4)	62.4	3 170	3 620	1 600	1.98	1.104
Diluted base water (1:4)	180.0	4 350	3 830	1 750	2.48	0.799
Diluted base water (1:4)	312.0	3 960	3 830	1 600	2.48	1.589

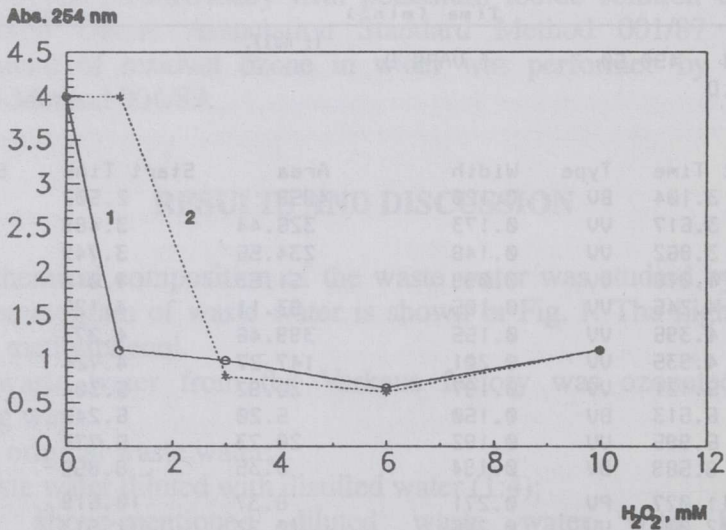


Fig. 2. The reduction of UV absorbance at 254 nm in the diluted waste water (1) and in the ozonated diluted waste water (2) by different dosages of hydrogen peroxide (the used ozone dosage was 170 mg/l).

The degrees of purification for COD and BOD are shown in Figs. 3 and 4. The COD and BOD values increased at first. The addition of hydrogen peroxide turns the initial compounds into compounds that are more easily decomposable. At further addition of hydrogen peroxide the values of COD and BOD started to decrease. The treatment of waste water with ozone and hydrogen peroxide leads to an efficient reduction of the organic compounds. The COD and BOD ratio was the smallest when the concentration of hydrogen peroxide was 3 mM.

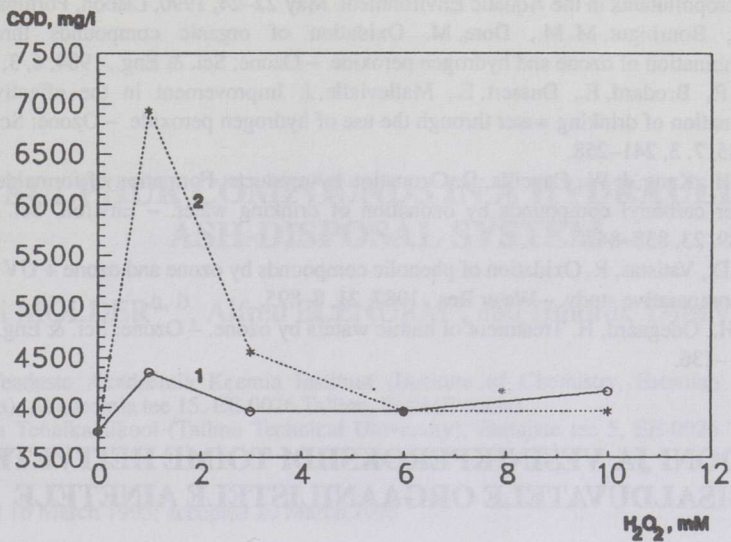


Fig. 3. The reduction in COD in the diluted waste water (1) and in the ozonated diluted waste water (2) by different dosages of hydrogen peroxide (the used ozone dosage was 170 mg/l).

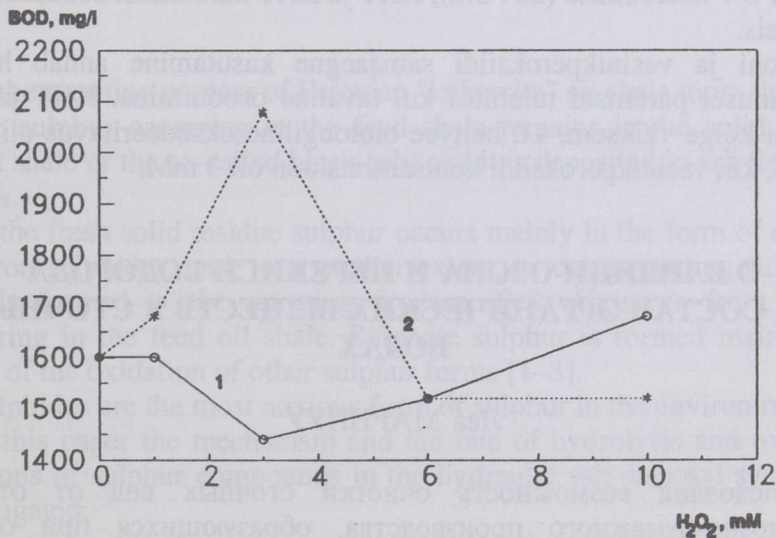


Fig. 4. The reduction in BOD in the diluted waste water (1) and in the ozonated diluted waste water (2) by different dosages of hydrogen peroxide (the used ozone dosage was 170 mg/l).

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OSOONI JA VESINIKPEROKSIIDI TOIME HEITVETES SISALDUVATELE ORGAANILISTELE AINETELE

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On uuritud võimalusi puhastada paberi- ja tselluloositööstuse puukoormistsehhi heitvett osooni ning osooni ja vesinikperoksiidiga. On jälgitud UV neeldumise (254 nm), KHT ja BHT muutumist oksüdatsiooniprotsessis.

Osooni ja vesinikperoksiidi samaaegne kasutamine annab heitvee puhastamisel paremaid tulemusi kui tavaline osoonimine. KHT ja BHT suhe oli kõige väiksem, s.t. heitvee bioloogiline oksüdeeritavus oli kõige suurem, kui vesinikperoksiidi kontsentratsioon oli 3 mM.

О ВЛИЯНИИ ОЗОНА И ПЕРЕКИСИ ВОДОРОДА НА СОСТАВ ОРГАНИЧЕСКИХ ВЕЩЕСТВ В СТОЧНЫХ ВОДАХ

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Исследована возможность очистки сточных вод от отходов целлюлозно-бумажного производства, образующихся при окорке древесины, озонном и системой, содержащей озон и перекись водорода. Проведено наблюдение за поглощением УФ-лучей (254 нм) и за изменением химического и биохимического потребления кислорода (ХПК и БПК соответственно) в процессе окисления.

Установлено, что совместное применение озона и перекиси водорода дает лучшие результаты при очистке сточных вод, чем обычное озонирование. Соотношение ХПК и БПК было наименьшим при концентрации перекиси водорода 3 ммоль (при наибольшей биологической окисляемости сточных вод).